Renewable and Sustainable Energy Reviews 23 (2013) 179–213

Contents lists available at SciVerse ScienceDirect

Renewable and Sustainable Energy Reviews

journal homepage: www.elsevier.com/locate/rser

Waste tyre pyrolysis – A review

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ARTICLE INFO

Article history:
Received 18 May 2012
Received in revised form
18 February 2013
Accepted 21 February 2013
Available online 27 March 2013

Keywords:
Waste tyre
Pyrolysis
Thermochemical processes
Renewable energy
Tyre recovery

ABSTRACT

This review deals with the state-of-the-art of waste tyre pyrolysis for the first time in literature. Pyrolysis has been addressed as an attractive thermochemical process to tackle the waste tyre disposal problem while allowing energy recovery. Pyrolysis enables the separation of carbon black from tyres and the volatile matter released (condensable and non-condensable compounds) has the potential of renewable energy recovery given the significant proportion of natural rubber present in the tyre. Given this waste-to-energy pathway, a comprehensive review has been carried out in order to show the effects of the main process conditions (heating rate, temperature, pressure, carrier gas flow rate and type, volatiles residence time and pyrolysis time) on the physicochemical properties and distributions of the resulting products (gas, liquid and solid fractions). It has also been reviewed the influence of the size and composition of the feedstock. All reported results have been framed regarding the type of reactor as well as the experimental conditions used to avoid contradictions among the large number of publications on the subject. It is shown that the occurrence of secondary reactions is very sensitive to the interaction of the aforementioned variables. Also, the main properties of the pyrolytic products are pointed out. The liquid and gaseous fractions obtained are a valuable fuel source; while the solid fraction (char) has the recovery potential of low- grade carbon black or as carbon adsorbent after applying an activation step. Special attention has been given to the liquid fraction, highlighting its properties as alternative fuel in compression ignition engines.

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Abbreviations: WT, waste tyre; NR, natural rubber; BR, butyl rubber; CB, carbon black; SR, synthetic rubber; SBR, styrene–butadiene rubber; TDF, tyre derived fuel; BTX, benzenes, toluenes and xylenes; BTXE, benzenes, toluenes, xylenes and ethylbenzenes; PAHs, polycyclic aromatic hydrocarbons; VOCs, volatile organic compounds; MSW, municipal solid wastes; DSC, differential scanning calorimetry; TG, thermogravimetric; DTG, differential thermogravimetric; BFBR, bubbling fluidised bed reactor; CFBR, circulating fluidized bed reactor; CSBR, conical spouted bed reactor; FBR, fixed bed reactor; AR, auger reactor; RKR, rotary kiln reactor; ICE, internal combustion engine; PCT, passenger car tyre; TT, Truck tyre; MT, motorcycle tyre; IEA, international energy agency; A, Ash; VM, volatile matter; FC, fixed carbon; M, moisture; CV, calorific value

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http://dx.doi.org/10.1016/j.rser.2013.02.038

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1. Introduction

The use of renewable sources and waste valorisation processes is increasing because of several factors, which include besides the global warming, the great dependence of society on fossil sources for both fuels and essential raw materials. On the other hand, the remarkable increase in the number of vehicles worldwide and the lack of both technical and economical mechanisms makes that waste tires are considered a serious pollution problem in terms of waste disposal. Since rubber from tires have a calorific value higher than coal as well as considerable amount of carbon black, it seems reasonable to find a route to take advantage of its high energetic and raw material potential in order to progress in the search of alternative fuels, CO_2 emission mitigation and the reduction/recycling on raw materials. Pyrolysis is receiving renewed interest and attention to tackle the waste tyre disposal problem while allowing energy recovery. Therefore, this work contains a thorough review of the governing variables influence on both yield and quality of the pyrolysis products, including the effect of both waste tyres types and pyrolysis reactor. The final target is to provide essential information to understand the pyrolysis process applied to waste tyres, including the physico-chemical properties of the products and their potential uses. Thus, this work has been divided into four parts. The first one shows some remarks about the waste tyres generation problem, the tyre compounds, the difficulties related in the waste tyre management and some current pathways for waste tyre recycling. The second part contains general information about pyrolysis and the characteristics of waste tyres as feedstock for this process. Types of reactors and different operation conditions for classifying the types of pyrolysis are also commented. Energy requirements and efficiency, as well as early works and advantages and disadvantages of waste tyre pyrolysis are also included. The third part is related with the governing variables in the tyre pyrolysis process (heating rate, temperature, pressure, carrier gas flow rate and type, volatiles residence time and pyrolysis time). Herein, special attention has been given to the temperature effect on the pyrolysis yields and three possible pyrolysis behaviours are proposed. The fourth and final part shows the properties of the tyre pyrolysis products framed regarding the experimental conditions used. Special attention is given to the liquid fraction, highlighting its properties as alternative fuel in compression ignition engines.

1.1. The waste tyres generation problem

New technologies, processes and resources are currently under research due to the current worldwide energy panorama. It is well-known that the high fossil fuel dependence and consumption of our society has driven to its depletion and to a negative impact on the environment mainly due to the global warming and the emission of harmful pollutants like SO_2, NOx and VOCs, among others. Parallel to this, there is a solid wastes disposal problem all over the world. Waste generation in the EU is estimated to stand at over 1.43 billion tons per year and is increasing at rates comparable to those of economic growth [1]. Although many of these residues are non-biodegradable materials, they are dumped because a lack of specific regulations and/or because the recycling is not economically attractive. Waste tyre (WT) falls into this kind of solid residues and it is managed as waste even if it is going to be recycled or re-manufactured. This is a burden that adds significant cost over disposal and in many cases acts as a barrier to improve resource efficiency [2].

About 1.4 billion new tyres are sold worldwide each year and subsequently just as many fall into the category of end-of-life tyres [2]. In units sold, which are somewhat less than those produced, passenger car tyres (PCT) account for slightly more than 90% whilst truck tyres (TT) and other categories constitute

the remaining 10% [3]. It is estimated that one car tyre per person is discarded each year in the developed world and hence 1 billion of WTs are disposed globally each year. Currently an estimated of 4 billion WTs are currently in landfills and stockpiles worldwide [1]. In 2010 the EU27 plus Turkey produced around 4.5 million tonnes of tyres, which represents 26.5% of the world tyre production (estimated at 17 million tonnes). From this amount, it is assessed that more than 3.2 million tonnes of WTs are discarded annually [2] and for this reason the disposal of WT is considered as an increasing environmental and economic problem [4]. On average, a brand-new car tyre weighs 11 kg and 9 kg when it is scrapped. Similarly, heavy tyres such as truck and bus tyres, weigh 54 kg new and 45 kg respectively [5].

The management of WT and in general of any waste, is intended to follow an hierarchical approach [6], that is, to decrease the environmental impact according to the ensuing order: waste minimisation, reuse, recycling, energy recovery, and landfilling [7]. The legislation related to waste management is demanding the search for economical and environmental mechanisms that can contribute to solve the waste disposal problem. WT disposal in landfills is banned in the EU [6], minimisation and reuse are options with limited applicability [7] and recycling cannot mitigate the disposal problem by itself. Therefore, energy recovery seems to have a high potential to process and to valorise WT [8]. Thermochemical processes such as pyrolysis, gasification and combustion offer important advantages from an energetic point of view to address this challenge.

1.2. *What is tyre made of?*

Tyres are made of rubber (60–65 wt%), carbon black (CB) (25–35 wt%) and the rest consists of accelerators and fillers, which are added during the manufacturing process The rubbery materials are present in the form of C_xH_y with some fibrous materials [9] and they are considered thermoset polymers. Vehicle tyres (both passenger and truck) are mainly a blend of natural (NR) and synthetic rubber (SR) such as butyl rubber (BR) and styrene–butadiene copolymer (SBR). The NR comes from the *Hevea* tree, whilst the SR is generally derived from petroleum-based products [3]. NR has unique elastic properties and it is an essential element of a tyre. Rubber comprises elastomeric polymers characterised by the presence of a network structure that can be temporarily deformed when subjected to external forces. According to the International Rubber Study Group [10] 24.37 million tons of rubber were produced in 2010. Of this amount, 10.38 million tons (42%) were NR and the remaining 13.99 million tons (58%) were SR.

The CB, an amorphous carbon of quasi-graphitic structure, is produced primarily by partial combustion of fossil hydrocarbons. It acts mainly to strengthen and to give abrasion resistance to the rubber. The remaining percentage is due to organic (about 7 wt%) and inorganic fillers (around 3 wt%) due to the addition of an extender oil (a mixture of aromatic, naphthenic and paraffinic hydrocarbons) in order to soften the rubber and to improve workability.

Generally speaking, it is possible to say that more than one hundred different compounds can be added to the tyre depending on the specific trademark and on the specific use to be given to the tyre [11,12]. The accelerators are usually added toward the end of the mixing cycle when the temperature of the mill or internal mixer is falling [13]. The tyre manufacturing process involves a vulcanisation process where an irreversible reaction among the elastomer, sulphur and other chemicals produces crosslinks between the elastomer molecular chains and the formation of a three-dimensional chemical network. The cross-linked elastomers are solid, insoluble and infusible thermoset materials [14], resulting in high strength and elasticity that makes the tyre decomposition difficult. Usually, the sulphur content of rubber from tyre is around or up to 1.5 wt% [12]. An accelerator, an organic-sulphur compound, is added together with ZnO and stearic acid, as a catalyst, to control the vulcanisation process and also to enhance the physical properties of the rubber [11,12,15,16]. Other inorganic compounds include clay fillers, calcium and magnesium carbonates and silicates as well as a variety of inorganic pigment materials [17].

1.3. *Why is tyre management difficult?*

Tyres are designed to withstand harsh mechanical and weather conditions as ozone (the most damaging factor on rubbers), light and bacteria, making difficult their recycling and/or further processing. Also they are bulky and do not degrade in landfills [9]. The tyre lifetime in a landfill is considered to be between 80 and 100 years. The fact that tyres are thermoset polymers means that they cannot be melted and separated into their chemical components [18].

Although initially WT does not represent an immediate danger, its inappropriate disposal or production in large quantities can seriously pollute the environment or cause problems when they are not properly treated. The storage of WT promotes the growth of pests and insects, causing not only a high risk of fire, which in turn can be difficult to extinguish, but also an environmental impact due to uncontrolled emissions of potentially harmful compounds into the atmosphere, soil and groundwater. In addition, it is also important to take into account the low bulk density of a whole tyre, since around 75% of its volume is an empty space that implies risk of toxicity and a potential storage of explosive gases if WTs are disposed in landfills.

Despite combustion can easily be used to recover energy, the emissions (dioxins, PAHs, VOCs, particulate matter, etc.) produced when complex wastes such as WTs are burnt make this possibility unfavourable from an environmental and public health point of view [11,12,19–23]. Both char and byproduct formations from an incomplete combustion also reduce fuel efficiency in combustion [24]. Furthermore, these compounds can also cross environmental media boundaries, transferring to soils, vegetation, water, etc. Consequently, human health can be also indirectly affected through different pathways such as drinking water or groundwater, skin absorption of the chemicals present in water, intake of contaminated foodstuffs and oral and skin absorption of chemicals from soils [23].

Since 1970s it has been reported that the combustion of rubber causes the emission of sizeable quantities of Zn particles [25]. Gieré et al. [22] found that atmospheric emissions of Zn increased from 15 g/h to nearly 2.4 kg/h when only coal and tyre at a ratio of 19:1 (wt%) were combusted. Similarly, emissions of most other metals and metalloids increased, as well as those of HCl (for a Cl content around 3000 ppm in tyre). Carrasco et al. [26] reported an increase of 47% and 30% in the rate of emissions of CO and SO_2 as well as a decrease of 15% for NOx when a plant of one million tons of cement per year was operated with a mixture of coal (80%) and tyres (20%). Moreover, inorganic compounds such as Zn, Cr, Pb, Mn, Fe and Al increased in comparison when only coal was used as feedstock. According to DeMarini et al. [27] the mutagenic emission factor of tyres burning in open air is 3–4 orders of magnitude greater than the values reported for the combustion of oil, coal or wood in utility boilers. A comparison between the PAHs emissions released under controlled conditions in the coal and tyre combustion carried out by Levendis et al. [19] showed that PAHs emissions from tyres were 1.5–2 times higher than those of coal at comparable equivalences ratios. This higher PAHs emissions could be attributed to the tyre structure and particularly to the CB, which has a high surface/weight ratio, serving as

support to PAHs deposition [28]. In the same way, the slow rate of the gas–solid reaction in the oxidation of the CB included in tyre could influence this behaviour [29].

1.4. Current pathways for waste tyre recycling

WTs have been widely used in many energy applications including power plants, tyre manufacturing facilities, cement kilns, and pulp and paper production among others [30]. These uses have demonstrated the capability to extract energy from the tyres in an environmentally acceptable manner [18]. According to Buekens [31] the major route for tyres is their use as supplemental fuel in cement kilns. The higher temperatures and longer residence time in a cement kiln must favour the tyre transformation, especially the combustion of CB. In addition, the cement production process can utilize the iron contained in the tyre steel beads and belts without changing the cement quality [18].

There are many studies on WT in cement kilns as tyre derived fuel (TDF) as reported in [26,32–35] and also as direct fuel in bubbling fluidised bed reactors (BFBR) operated as combustors [36] and gasifiers [37–40]. Accordingly, Singh et al. [41] showed the feasibility of using TDF as secondary fuel in thermal power plants to reduce the use of coal and NOx emissions. Giugliano et al. [33] pointed out that blends of WT/coke in cement kilns do not require major modifications in the operation and layout of the plant. The authors also detailed some process conditions regarding temperature and residence time of combustion gases in order to ensure a good operation performance for the clinker production.

Likewise, the US Environmental Protection Agency (EPA) recognises the use of TDF as a viable alternative to the use of fossil fuels and supports the responsible use of tyres in Portland cement kilns and other industrial facilities such as pulp and paper mills, electric utilities and industrial/institutional boilers, so long as meet the management and environmental requirements framed by legislation [42]. TDF represented 54% (around 2.5 million tons) of the total scrap tyres generated in US in 2007 (about 4.6 million tons) [5]. The cement sector is the main user of TDF. The main benefits in using tyres and in general solid wastes in cement kilns include energy recovery, conservation of non-renewable fuels, reduction in cement production costs and the use of already existing facilities, among others [23].

Other fields for tyre recycling are civil engineering, in concrete and asphalt manufacture or roofing applications [43–46]. Also, they are used in rubber engineering as a filler for virgin and devulcanised rubber blends and for the production of shoe heels and soles, tubes, conveyor belts, automobile floor mats, flaps, etc. [47]. Recent uses and management strategies for tyre rubber recycling can also be found elsewhere [48,49].

2. Waste tyre pyrolysis

2.1. Waste tyre as feedstock for pyrolysis

The proximate analysis of any fuel gives its amount of moisture, volatile matter, fixed carbon and ash. It has been reported that the volatile matter of the tyre consists mainly of polymeric compounds that come from NR and SR, whereas the fixed carbon should match with the CB used in tyre manufacturing. Thus, the amount of volatile matter should correspond to the amount of gas and liquids to be obtained in the pyrolysis process, whilst the amount of non-volatile matter should coincide with the solid residue remaining after pyrolysis [50]. Vehicle tyres (PCT

Table 1
Elemental and proximate analysis, and calorific value of different tyres reported in literature.

Elemental analysis on dry basis (wt%)						Proximate analysis on as received basis (wt%)				CV (MJ/kg)	Ref.
C	H	N	S	O	A	A	VM	FC	M		
81.72	6.54	0.55	1.87	2.68	6.64	6.64	62.58	30.07	0.71	n.r.	[8]
83.80	6.90	0.60	2.00	2.30	4.40	4.30	63.40	30.40	1.90	n.r.	[36]
83.80	7.60	0.40	1.40	3.10	3.70	3.70	67.30	28.50	0.50	36.45[a]	[39]
82.36	6.92	2.30	1.40	2.03	5.00	4.95	73.74	20.22	1.09	37.06[b]	[40]
75.50	6.75	0.81	1.44	15.50[c]		20.10	57.50	20.85	1.53	29.18[a,g]	[51]
85.90	8.00	0.40	1.00	2.30	2.40	2.40	66.50	30.30	0.80	40.0[a]	[52]
75.40	7.03	0.21	1.62	5.09	10.21	10.21	62.32	26.26	1.31	33.29[a]	[53]
84.33	7.81	0.49	1.66	3.32	2.40	7.10	62.20	29.40	1.30	40.0[a]	[54]
82.80	7.60	0.50	1.30	4.50	3.30	3.30	68.70	27.20	0.80	36.46[a]	[55]
86.70	8.10	0.40	1.40	1.30	2.10	8.00	61.90	29.50	0.70	36.20[a]	[56]
80.29	7.25	0.31	1.84	4.90	5.41	5.30	67.50	25.20	2.10	37.30[b]	[57]
85.05	6.79	0.50	1.53	1.75	4.40	4.35	62.24	32.28	1.14	34.90[a]	[58]
81.50	7.10	0.50	1.40	3.40	6.10	6.07	64.87	28.56	0.50	36.80[a]	[59]
86.09	6.74	0.19	1.93	1.35	3.70	3.70	65.50	29.40	0.90	n.r.	[60]
86.70	6.90	0.30	1.90	0.90	3.30	4.40	64.00	30.70	0.90	31.80[b]	[61]
83.92	6.83	0.78	0.92	3.39	4.16	4.16	64.97	30.08	0.75	38.6[a,e]	[62]
85.25	7.94	0.41	1.38	1.19	3.83	3.83	64.09	31.14	0.94	n.r.	[63]
83.00	6.79	0.32	1.37	3.46	5.06	5.00	64.10	29.70	1.20	35.00[b]	[64]
67.08	6.12	0.17	2.05	24.58[c]		19.10	59.69	19.45	1.72	27.37[a]	[65]
81.79	7.99	0.48	1.81	3.04	4.90	4.88	65.74	28.98	0.40	38.30[a,d]	[66]
84.00	7.19	0.49	1.42	3.30	3.60	3.60	65.60	30.00	0.80	38.80[a]	[67]
83.15	6.78	0.28	1.77	0.84[d]	7.10	7.10	61.90	29.90	1.10	37.35[a]	[68]
74.30	7.20	0.90	1.71	15.89[c]		18.90	58.20	21.30	1.60	30.50[a,e]	[69]
83.20	7.70	1.50	1.44	6.16[c]		5.00	66.10	27.50	1.40	33.40[a,f]	

n.r., not reported; A, ash; VM, volatile matter; FC, fixed carbon; M, moisture.

[a] Higher.
[b] Lower.
[c] Including ash.
[d] Mixture between passenger car and truck tyres.
[e] Passenger car tyre.
[f] Truck tyre.
[g] Motorcycle tyre.

and TT) have a high calorific value (35–40 MJ/kg), even greater than the most of conventional coal used in power plants (around 25–50%). Motorcycle tyre (MT) has a lower calorific value that normally does not exceed 30 MJ/kg due to the lower volatile fraction (~58 wt%) as well as the higher ash content (~20 wt%) for this type of tyre [51].

A compendium of proximate and elemental analysis of rubber tyre reported by several authors is shown in Table 1 (on a steel free basis). As it can be observed, the ash content varies in the range between 2.40 and 20.12 wt%, the volatile matter varies between 57.50 and 73.74 wt% and the fixed carbon ranges from 19.45 to 32.28 wt%. These differences regarding the proximate analysis among different tyre brands can affect the pyrolysis product yields, as it will be shown below. As pointed by Mastral et al. [20], although tyres and coal are materials with different nature, the substantial difference lies in the moisture and ash content, which is usually greater for coal. Regarding the elemental analysis, it can be appreciated that there are some differences for the contents of C and S, whereas for the N and H contents the values are very similar.

2.2. The pyrolysis process

Pyrolysis has been used to produce charcoal from biomass for thousands of years. Pyrolysis of coal and biomass (mainly wood) was used commercially for the production of fuel gas and for smokeless solid fuel from the 1700s to early 1900s [70]. Traditional earthen, brick and steel kilns typically vent volatiles to the atmosphere during the charcoal production and for this reason some of these industries have a bad environmental reputation [71].

Pyrolysis, also termed thermal distillation or thermolysis is a thermochemical treatment that allows breaking apart chemical bonds [72] by means of a thermal decomposition under non-oxidative conditions (inert atmosphere or vacuum) and it is also the first step in any gasification or combustion process. Semantically the term thermolysis is more appropriate than pyrolysis since *pyro*, the Latin word for fire, implies the presence of oxygen and hence of reactive and oxygen-bearing intermediates [31]. Pyrolysis has been also referred as a reverse polymerisation, thermal depolymerisation or polymer cracking. From the recycling point of view, the main advantage of the process is that it can deal with wastes, which are otherwise difficult to recycle, and consequently, can create reusable products [73].

This thermochemical treatment can be used for feedstock recycling transforming solid wastes into high calorific fuels, chemicals, monomers or other valuable materials. In the case of solid materials, pyrolysis releases high-energy-density volatile gases (condensable high-molecular-weight compounds and non-condensable low-molecular-weight products known as pyrogas or syngas) and a high-energy-density carbonaceous solid known as char or pyrolytic CB where most of the fixed carbon and ash are trapped. Essentially, pyrolysis involves the heating of the feedstock to temperatures higher than 400 °C in the absence of oxygen, in an inert or a self-generated atmosphere, leading to the volatilisation and the decomposition of the different structures that compound the feedstock. When a feedstock is heated under those conditions, many reactions including dehydration, cracking, isomerisation, dehydrogenation, aromatisation and condensation take place [70]. According to Scheirs [74], albeit pyrolysis of wastes appears simple in concept, the products are often low-value mixtures of hydrocarbons with a very broad compositional range, sometimes extending from light alkane gases to coke. For this reason depending on the final objective of the pyrolysis, it is necessary to find the optimal conditions for the type of feedstock and the process characteristics such as particle size, temperature, reaction time, heating rate, type of atmosphere and its flow rate, etc.

2.3. A waste tyre pyrolysis reaction scheme

Generally speaking, polymers are structurally made up of carbon atoms linked by single or double bonds [75]. Dodds et al. [17] reported that rubbers are characterised by carbon–carbon double bonds, and that thermal decomposition produces highly reactive free radicals, which are often sub-units of the original rubber molecule. Aguado et al. [76] also described the thermal degradation process according to a radical chain reaction pathway comprising hydrogen transfer steps along with the progressive breaking of the polymer backbone. In addition to those generic reaction pathways, works on detailed mechanisms have been also reported in order to explain rubber pyrolysis reaction. For instance, Groves et al. [77] studied the thermal degradation of NR by pyrolysis-gas chromatography at 500 °C. They suggested that monomer recombination, possibly by a Diels–Alder mechanism, is an important contributor to dimer formation in rubber pyrolysis. Similarly, Mastral et al. [12] also suggested a possible reaction pathway for rubber tyre conversion through polyisoprene depolymerisation and further cyclisation. Pakdel et al. [78] proposed that the polyisoprene of the rubber thermally decomposes through a β-scission mechanism to an isoprene intermediate radical. Then, it is transformed to isoprene (depropagation) and these isoprene molecules in the gas phase dimerise to dipentene. More recently, Kwon and Castaldi [79] reported that the thermal degradation mechanism of WT takes place via bond scission on each monomer of the main constituents of tyres, followed by hydrogenation and recombination by gas phase reaction.

From a general point of view, it is possible to say that WT pyrolysis involves intramolecular free radical reactions that change with the pyrolysis conditions. Although each individual reaction is difficult to determine, Li et al. [58] classified the reactions involved in tyre pyrolysis into three groups: primary pyrolysis reaction (250–520 °C), secondary post-cracking reaction of pyrolytic volatiles (600–800 °C) that strongly affect BTX yields,

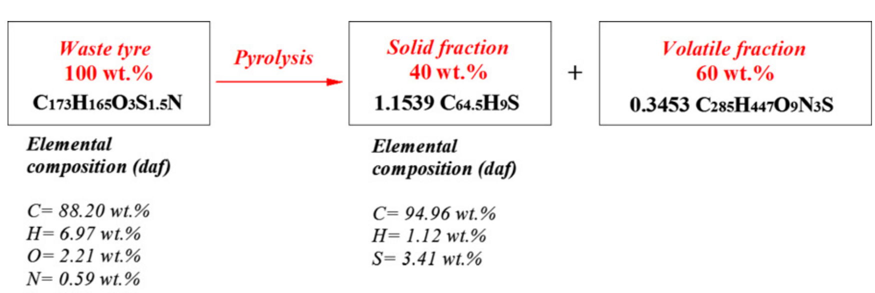


Fig. 1. Tyre pyrolysis process as elemental reaction.

and pyrolytic CB gasifying reaction with $CO_2/H_2O/O_2$ in the gases (750–1000 °C). According to the authors, the importance of each reaction group is dependent on two parameters: the temperature and the reaction time, as indicated by the rates of reaction in the Arrhenius equation.

In spite of the fact that pyrolysis follows complex routes that strictly cannot be described by one or more chemical reactions, an empirical formula based on the mass conservation law enables a workable and feasible pyrolysis reaction scheme [31]. During pyrolysis, WT is decomposed to form a solid carbonaceous fraction and volatile products. In this sense, assuming a solid conversion of 40 wt% and that only the organic fraction contained in the tyre interacts in the pyrolysis reaction, the process can be expressed from the elemental analysis of tyre and pyrolytic CB, as the scheme showed in Fig. 1. From this approach and also taking into account the reaction enthalpy of the tyre, it is possible to develop an energy balance to determine the energy content of the volatile fraction.

2.4. Reactors for pyrolysis

According to Scheirs [74] plastic pyrolysis and/or catalytic cracking processes are generally carried out in continuous stirred tank reactors. Industrial plants have a floor with conical or torispherical shape with a volume ranging from 3 to 20 m^3. However, for tyre pyrolysis, the panorama is wider being possible to find laboratory and pilot plant scale, from autoclaves, rotary kilns, screw conveyors (auger), fixed, spouted, entrained and fluidised beds, rotating cone, vortex reactor, melting vessels, plasma reactors, free-fall, tubing bomb reactors, to vacuum pyrolysis and the ablative process, among others (Table 4 shows more details about these reactors). All these reactors/configurations have advantages and disadvantages in terms of technical, economical and ecological parameters and are used for different energy applications such as distributed generation (heat and/or electricity) and/or the production of liquid fuels and char.

A significant number of technological equipments with different configurations and layouts have been proposed, designed and tested. Meier and Faix [80] highlighted the most relevant reactor designs for fast pyrolysis aiming the liquid fraction production: the BFBR and CFBR, the ablative process (the rotating cone and vortex reactor) and the vacuum pyrolysis. Also, Malkow [81] presented a comprehensive review about novel and innovative pyrolysis and gasification technologies for MSW disposal with energy recovery. Different configurations for MSW processing (including WT and rubber materials) by means of those thermochemical processes combined with combustion processes in different types of reactors were also shown.

Similarly, Mohan et al. [82] presented a large review on pyrolysis of wood/biomass for bio-oil production. Herein the authors also explain several reactors and processes configurations for conducting biomass pyrolysis that can also be used for tyre pyrolysis as reported by Roy et al. [83]. Technologies are similar regardless of the feedstock albeit some changes may be needed regarding to the feeding system. Likewise, the authors highlighted the main technologies available for the pyrolysis commercialisation with acceptable yields of liquid products: BFBR and CFBR, vacuum and ablative processes, and auger reactor (AR). At industrial scale the rotary kiln reactor (RKR) and the fluidised bed reactor are the most attractive. Usually, each type of reactor offers certain particularities in the heat transfer process and processing capacity. All these characteristics have a remarkable influence in the pyrolysis process and in the product distribution. For instance, a higher heating rate enhances bond breaking and could lead a higher liquid yield as well as a secondary reactions reduction. Even so, depending on the volatiles residence time, it is possible to find an increase in the char yield at the expense of liquid formation, as a consequence of the occurrence of those secondary reactions. More details about this process conditions are presented in the next section.

2.5. Types of pyrolysis

There are many classifications of types of pyrolysis depending on the operating conditions, such as the heating rate, the volatiles residence time and the temperature. Thus, it is possible to have a general simple classification as slow and fast (this last one sometimes called also as flash, albeit this term can also mean higher heating rates and shorter vapour residence times than the fast pyrolysis). Pyrolysis can be also classified on the basis of the environment used such as oxidative pyrolysis, hydro-pyrolysis, steam-pyrolysis, catalytic-pyrolysis and vacuum pyrolysis, and also depending on the heater system as the microwave or plasma pyrolysis. Conventionally, fluidised and entrained beds reactors are associated with fast pyrolysis whilst fixed bed reactors (FBR) with slow pyrolysis (a batch or semi-batch process). However, it is worth noting that it is possible to perform fast pyrolysis in FBR adjusting the heating rate and the volatiles residence time for research purposes. Other types of reactors such as the AR and the rotating cone (usually used for liquid production since the heating rate is high and the vapour residence time is relative short), may also be categorised for carrying out fast pyrolysis.

2.5.1. Slow pyrolysis

This type of pyrolysis, as the name suggests, considers a slow pyrolytic decomposition at low temperatures. Slow pyrolysis is characterised by low heating rates, relatively long solid and vapour residence times (in the order of minutes to hours) and sometimes by low temperature. Longer residence times result in leading secondary conversion of primary products, yielding more coke, tar, as well as thermally stable products [31]. This fact makes the slow pyrolysis also be termed carbonisation. Unlike fast pyrolysis, the objective of the slow pyrolysis is the char production, although tar and gases are also obtained but not necessarily recovered.

2.5.2. Fast pyrolysis

Contrary to slow pyrolysis, fast pyrolysis implies a rapid thermal decomposition categorised by higher heating rates. This process usually requires a feedstock with small particle sizes and devices with special design to allow removing the vapours released quickly. High heating rates with short hot zone residence times and rapid quenching of the products (volatiles) favour the formation of liquid products, since the volatiles released in the pyrolysis process are condensed before further reaction breaks down the higher molecular weight species into gaseous products [54]. Thus, a liquid fuel with a higher calorific value is obtained. In fact, fast pyrolysis is recognised as an effective conversion route for the production of liquid fuels, chemicals and derived products with higher yield (usually around 50–60 wt% for rubber feedstock).

Fast pyrolysis is usually performed in fluidised beds, entrained, ablative and free-fall reactors where the reaction time is of the order of milliseconds to seconds. It is generally accepted that the volatiles residence time must be lower than 2 s [84]. Longer residence times result in significant reductions in organic yields resulting in the occurrence of secondary reactions as thermal cracking. Ultrapyrolysis, or ultra rapid pyrolysis, refers to thermal cracking under conditions of high temperature (in excess of 700 °C), very short reaction time (much less than 500 ms), higher heating rate (greater than 1000 °C/s) and rapid product quenching [85].

2.5.3. Catalytic pyrolysis

Normally, catalytic pyrolysis is the name given to any pyrolytic process that comprises a catalytic material in the same process in order to favour or upgrade some yield or some properties of the products. Catalytic pyrolysis of WT has been conducted for the production of single ring aromatic compounds in the liquid fraction such as benzene, toluene and the *m*-, *p*- and *o*-xylenes using zeolite catalysts (Y-type and ZSM-5) [86]. Likewise, Kar [65] found an enhancement of the liquid fraction yield and its fuel properties using an expanded perlite as catalyst. A catalyst to tyre ratio of 0.1 led an increase of 8.48 wt% of the liquid fraction compared with the non-catalytic pyrolysis. In the same way, Zhang et al. [62] revealed that the NaOH addition favoured lower pyrolysis temperatures. The authors achieved 49.7 wt% of liquid yield at 480 °C as well as a remarkably increase of H_2 in the gas fraction. Similarly, a considerable increase of the gas yield at expense of the liquid yield was also reported by Dung et al. [87] using Ru/MCM-41 as catalyst. In addition, higher yield to light olefins (4 times higher than non-catalytic pyrolysis) was also obtained. Elbaba et al. [88] observed a high increase in H_2 and CO concentrations as well as an marked decreased in CH_4 and C_2–C_4 concentrations when WT was submitted to a two-stage pyrolysis-gasification process at 500 and 800 °C respectively, in presence of a Ni–Mg–Al (1:1:1) catalyst.

2.6. Energy requirements and efficiency of pyrolysis

The energy necessary for developing the pyrolysis process, sometimes termed as enthalpy or heat for pyrolysis, is defined as the energy required to raise the feedstock from room temperature to the reaction one (sensible energy) and also the energy to convert the original feedstock into the pyrolysis products (reaction enthalpy) [89]. The heat demand, in the strict pyrolysis process, can be supplied by different heat sources: (i) by burning an auxiliary fuel, (ii) by burning the gas and/or solid fraction obtained in the process, (iii) by electric heating and (iv) by using hot sand, solvents or molten salts as a heat transfer medium (heat carriers).

Although WT pyrolysis is an overall endothermic process, it involves a series of endothermic and exothermic reactions [90–93]. Yang and Roy [91] studied the enthalpy changes during rubber pyrolysis as a function of temperature over the complete pyrolysis conversion range. They revealed an exothermic reaction ascribed to the chemical reactions involved at the early stage of the process as well as an endothermic reaction attributed to the vaporisation of the pyrolysis products. As mentioned by Cheung et al. [93], at the beginning of the pyrolysis process organic matter is primarily cracked down into small fractions and this reaction is exothermic. As the process temperature increases, some of the primary products are cracked down to secondary products and vaporised. The secondary cracking and vaporisation are usually summarised as endothermic reactions. In spite of these facts, the endothermic reactions dominate the energy requirement of the pyrolysis process.

According to Dodds [17], the net energy balance for WT pyrolysis suggests that the energy recovery is about 75–82% based on the heat of combustion of the tyre. Laird et al. [71] stated that the energy efficiency of pyrolysis often involves the major product of the process as a function of its marketability, although it can be apportioned among all products. The authors also pointed out that the energy efficiency can take into account the energy associated with the feedstock production. This is, for the tyre case, the energy required for NR, SR and CB production, as well as the consumptions in transport among others. A complete life cycle assessment would include these energy costs as well as the energy required to fabricate the pyrolysis equipment and to erect and to maintain the plant [71].

Among all the energy demands involved in pyrolysis, the reaction enthalpy is the most representative since it is used to carry out the process. However, there are several values reported for this parameter for the rubber tyre case. Gomez et al. [94] stated that secondary reactions between volatiles and char, as well as autocatalytic effects due to impurities, are usually assumed to be the reasons for the wide variation of values reported in the literature for the heat requirements of the pyrolysis process. Also, the differences among all type of tyres regarding its composition are not negligible. Under this context, Aguado et al. [92] reported a reaction enthalpy for the rubber tyre sample used of 267.6 kJ/kg. In the same way, the overall enthalpy change (endothermic) for NR and SBR from 30 to 510 °C reported by Yang and Roy [91] was 870 and 550 kJ/kg respectively. Cheung et al. [93] found different reaction enthalpies for different heating rates and reaction temperatures. For example, these authors reported a value of 646 kJ/kg at 20 °C/min and 510 °C. They also stated that lower heating rates require less energy to complete the pyrolysis, but a longer completion time. In contrast, higher heating rates need more energy to complete the pyrolysis but have a shorter completion time. It can be concluded that although the energy required to drive the tyre pyrolysis is highly heterogeneous, it is worth noting its low value in comparison to the heat of combustion of the tyre (35–40 MJ/kg) as well as the values of the products derived after pyrolysis (volatile and solid fractions around 42 and 31 MJ/kg respectively).

2.7. Early works on tyre pyrolysis

Midgley and Henne studied the destructive distillation of rubber in a series of 18 papers during the late 1920s and early 1930s. They found that isoprene and dipentene were the dominating products of the rubber distillation [95]. According to Dodds et al. [17] a large number of WT pyrolysis projects with a broad range of process technologies had been carried out at laboratory, pilot-plant and small commercial scale in the US, Japan, UK and Germany since late 1960s. A comprehensive description of the pyrolysis process characteristics implemented by the different companies and institutes in the aforementioned countries can be found elsewhere [17,18,25,58,96–98].

From an industrial point of view, several authors [18,25,99] pointed out that pyrolysis of WT was first attempted by the US Bureau of Mines in collaboration with the Firestone Company in the US in the early 1970s. A 10 tyre per day laboratory unit was developed with a production of 3.8 l of liquid. 3.2 kg of char, 1.4 kg of gas and 1 kg of steel and char per tyre pyrolysed [18]. According to Buekens [25] the apparatus consisted of an externally heated, sealed, bench-scale retort, which was normally used for studying the coking of coal. The volatile products passed through various cleaning devices such as condensers, electrostatic precipitators and acid and caustic scrubbers. Lately, since 1970s, the interest in pyrolysis grew over the world and a large quantity of patents for tyre processing and other type of wastes can be found as shown in Table 2. All these patents seek the recovery of valuable compounds, highlighting the thermochemical process of pyrolysis as an alternative for wastes disposal with energy recovery.

In the scientific field, between 1970s and 1980s, WT pyrolysis studies were intensified and several reactors and process layouts were proposed [47,90,96,100–107]. Many of these works were also mentioned by Li et al. [58] in a short review regarding some remarkable conclusions obtained from WT pyrolysis studies carried out in laboratory and pilot scale units such as fluidised beds, vacuum moving beds, two-stage moving beds, ablative beds

Table 2
Patents' summary for tyre and waste recovery in the 1970s and 1980s.

Patent's name	Patent's code	Year	Authors	Company	Country	Brief explanation of the invention	Ref.
Hydroconversion of waste natural and synthetic rubbers	US 3704108	1972	Alpert	Hydrocarbon Research Inc	US	Wastes rubbers conversion in the presence of a catalyst under hydrogen atmosphere. Operation temperature and pressures ranging from 372 to 454 °C, and 3447 to 20685 kPa g respectively. A hydrocarbon liquid and a carbonaceous solid was the aim of the invention	[119]
Recovering carbon black from waste rubber	US 3978199	1976	Maruhnic et al	Hydrocarbon Research Inc	US	CB is recovered from vulcanised waste rubber by reacting with an aromatic liquid solvent in a stirred reactor at 260–372 °C and about 172–690 kPa g for 0.5–2 h. The resulting solids–liquid mixture is processed to remove solids, and the resulting solid product is then dried, screened and chemically treated to recover the CB in dry powder	[120]
Scrap-tire feeding and coking process	US 4030984	1977	Chambers	Deco Industries	US	Process and apparatus for the recovery of carbonaceous raw material from scrap tyre. Hot gases between 122 and 315 °C melted the tyres allowing the recovery of the carbonaceous raw material as well as a liquid and a gas fraction	[121]
Production of a char reinforced agent from pyrolyzed scrap-tyre	US 3823224	1974	Laman and Kay	The Firestone Tyre & Rubber	US	Production of a rubber reinforcing agent derived from vulcanised scrap rubber. Scrap rubber is charred by heating with substantial absence of air from 538 to 1370 °C and then treated with acid to remove metal compounds. The product has been found to be a very satisfactory rubber-reinforcing agent	[122]
Pyrolization	US 3966487	1976	Crane and Kay	The Firestone Tyre & Rubber	US	Process for the recovery of the CB from scrap-rubber. The scrap is continuously pyrolysed to produce a product composed largely of CB originally present in the scrap. After grounding it. CB may be used as a reinforcing agent	[123]
Reinforcing agent from scrap rubber char	US 3644131	1970	Gotshall	n.r.	US	PCTs are subjected to destructive distillation under N_2 atmosphere at approximately 900 °C. The resulting gases are burned to heat the retort, the liquid product is condensed and retained. The solid char is grounded under non-oxidising atmosphere and the particles are protected from oxygenation of their surfaces until they have been coated with an organic liquid	[124]
Microwave pyrolysis of wastes	US 3843457	1974	Grannen et al	Occidental Petroleum Corp.	US	After separation of the organic and inorganic compounds, wastes are shredded to a fine particle size and subjected to microwave discharge in the low gigahertz frequency range. Vapourised products are rapidly swept from the pyrolysis zone and passed to separation stages where various organic products are collected	[125]
Char composition and a method for making a char composition	US 4038100	1977	Haberman	The Oil Shale Corporation	US	A solid char material with a very fine particle size is produced from rubber pyrolysis with heated balls for a sufficient time to vaporise and depolymerise the hydrocarbons. The char is free of nondecomposed rubber and coke. The resulting char may be used, among other things, as a substitute for CB in the production of various products such as tyres	[126]
Apparatus and method for the pyrolysis of solid waste material	US 3768424	1973	Hage	Mechtron International Corporation	US	Method and apparatus for the disposal of solid material, using a pyrolytic decomposition chamber for heating the material to its decomposition temperature in absence of air	[127]
Rubbers reinforced by scrap rubber char	US 3772242	1973	Liska et al	The Firestone Tyre & Rubber Company	US	Scrap synthetic rubber is destructively distilled (at around 500 °C) to produce a char that may be used in the reinforcement of rubbers. Valuable liquid and gas are also obtained	[128]

Table 2 (*continued*)

Patent's name	Patent's code	Year	Authors	Company	Country	Brief explanation of the invention	Ref.
Method and apparatus for the pyrolysis of waste products	US 4084521	1978	Herbold et al	Helma Lampl	Germany	Apparatus and method for the pyrolysis of waste material such as WTs. The material is fed to the reactor and heated under sub-atmospheric pressure by an outside heat source, the decomposition products being given off mainly in the form of gases. Some of the gas fraction is burnt to provide the heat	[129]
Method for recycling tyres and similarly compounded materials to recover usable constituents	US 4240587	1980	Letsch	n.r.	Germany	A processing plant and method for treating scrap tyres and similar materials. The plant is essentially vehicular and thus eliminates the necessity of hauling accumulated tyres long distances with the accompanying costs. Tyres are pyrolised after a size particle reduction	[130]
Apparatus for the pyrolysis of pieces of rubber or like material. especially used motor vehicle tyres	US 4203804	1980	Janning et al	Carl Robert Eckelman Ag.	Germany	A BFBR for the pyrolysis of pieces of rubber materials, especially WTs	[131]
Apparatus for the production of combustible gas	US 4142867	1979	Kieneer	n.r.	Germany	Apparatus for the production of combustible gas from waste materials and other materials. It is essentially at low-temperature carbonisation (from 300 to 600 °C) process without air. The resulting solid residues are separated and the gases released are continuously drawn through a reaction bed at a temperature of from 100 to 1200 °C	[132]
Process for hydrocracking a waste rubber	US 4251500	1981	Morita et al	Bridgestone Tyre Company Limited	Japan	Process for hydrocracking a waste rubber (WTs, waste conveyor belts. waste hoses, etc.) with a specific catalyst favouring its decomposition into a liquid and solid carbonaceous material	[133]
Process and apparatus for heating solid materials containing volatile matters	US 4140478	1979	Kawakami et al	Kobe Steel. Ltd.	Japan	Process and an apparatus for heating solid materials containing volatile matters. Granulated WT is supplied at a feed rate of 100 kg/h into a conventional RKR, and then subjected to thermal decomposition at 650 °C to obtain CB	[134]
Pirolyzing apparatus	US 4324620	1982	Ito et al	Ebara Corporation	Japan	Apparatus having a pyrolysis fluidised bed chamber and an incineration fluidised bed chamber	[135]
Apparatus for treatment of rubber and plastic wastes	US 4208252	1980	Yoshida et al	Sumitomo Chemical Industries Ltd.	Japan	Apparatus and method for pyrolysis and liquefaction of rubber and plastic wastes by means of an extruder. Temperature in extruder is low from 100 to 400 °C. Temperature in decomposing duct is about 400 °C or up to 1000 °C.	[136]
Process for producing hydrocarbons	US 4214110	1980	Moroe et al	Takasago Perfumery Co. Ltd.	Japan	Process for producing hydrocarbons having about 10–50 carbon atoms with a high yield by subjecting a synthetic polyisoprene rubber to a thermally destructive distillation under a reduced pressure	[137]

n.r., not reported.

and rotary kilns. Representative results and process characteristics of those works are briefly commented below.

The Kaminsky and coworkers studies carried out at the University of Hamburg [100–103] were mainly focused on the feasibility demonstration of tyre and other plastic feedstock pyrolysis in a BFBR with and without tyre size reduction. Three-step scale-up facilities (laboratory plant 100 g/h, pilot plant 30 kg/h and prototype plant 150 kg/h) were tested. In the prototype plant, product yields were 18–25 wt% of gas, 25–30 wt% of liquid, 35–45 wt% of char (CB and filler material) and 8–12 wt% of steel cord when 1500 kg of whole tyres (over 150 tyres) were processed in one run. CH_4 and C_2H_4 were the main gases in the gas fraction whilst the liquid presented an aromatic nature. Buekens [31] highlighted the work developed in Hamburg as pioneering in Western Europe since its inception in 1970s using several types of plastic as feedstock.

Kawakami et al. [47] also demonstrated the technical feasibility for tyre pyrolysis in a RKR with 1100 kg/h of nominal capacity. The pyrolysis time (residence time of the feedstock in the reactor) was about 15 min [25]. The volatile products entered in a cooling tower where they were separated into liquids and gases. Gases, after caustic scrubbing, were used for heating the kiln. The maximum liquid yield was 53.0 wt% achieved at 500 °C. Collins et al. [90] conducted TG and DSC studies carried out under atmospheric and vacuum conditions. They reported that the thermal degradation process of tyre starts about 225 °C at atmospheric pressure while it starts about 150 °C at vacuum pressure. They also revealed the presence of both endothermic and exothermic reactions. Fletcher and Wilson [96] from Foster Wheeler proposed a cross-flow system for tyres pyrolysis claiming the need of attaining an intimate gas–solid contact and hence

a high-efficiency heat transfer. According to them, a 1 t/d pilot plant based on this concept produced a gas and liquid fraction adequate for the thermal requirements of the system. Lucchesi and Maschio [104] carried out tyre pyrolysis studies in a counter-current FBR and found that pyrolysis gases had enough energy to supply the energy demand of the process. They also noted that the liquid fraction had a high percentage of aromatics, whilst the solid fraction could be used as a precursor for activated carbons. Works using a special solvent composed of heavy oil to dissolve oligomers formed by devulcanisation and depolymerisation were also carried out by Bouvier and Gelus [105]. Products derived included a combustible gas and a liquid fraction, as well as an oil–CB suspension. Process temperature was around 380 °C. Also, kinetic studies from TG analysis were reported in 1980s according to the works of Bouvier et al. [107] and Boukadir et al. [108]. The former showed that thermal degradation of tyre proceeded in two steps according to their main compounds: the polybutadiene cracked at lower temperatures (below 300 °C) than the polystyrene (between 300 and 450 °C). The last work revealed the parameters involved in the Arrhenius equation and found that rubber degradation is a one-step mechanism that follows a first order reaction.

Vacuum pyrolysis process of different feedstocks including WT has been under development at the Université Laval in Canada since the early 1980s [83,109]. The research program led by Roy and coworkers focused on establishing background knowledge about the reaction mechanism, pyrolysis product characterisation and design and operation of process-development units with capacities ranging from batch systems to an industrial-scale demonstration plant with a throughput capacity of 3 t/h [13,83,109,110–116]. Moreover, in 1990s Williams and coworkers at the University of Leeds [4,15,52,54,117,118] intensified the study on tyre pyrolysis in FBRs providing interesting information regarding the process as well as a complete characterisation of the products.

Since then, there has been a large papers production on the subject in several countries around the world. During the past decade feedstock recycling of plastic wastes by thermal and catalytic process such as pyrolysis has undergone an important evolution and some commercial processes have been developed worldwide, for the production of both liquid fuel [7] and char [4]. Nevertheless, the current experiences for both pilot/demonstration and industrial plants are relatively few over the world. The main reason is the lack of exploitation for the solid fraction that directly affects the economic feasibility of the process.

2.8. Tyre pyrolysis advantages and disadvantages

According to several authors [8,63,138,139] WT pyrolysis seems to be more attractive in comparison with other thermochemical processes because of its minor environmental impact and the recovery of solid and liquid material. Combustion–incineration is primarily distinguished as a destructive process and this fact makes that pyrolysis is recognized as efficient method for waste valorisation. WT pyrolysis products are easily manageable and then valorised separately according to different objectives. The production of a liquid fuel, the major product in WT pyrolysis, increases the ease of handling, storage and transport and hence the product does not have to be used at or near the recycling plant [4,54]. On the other hand, the volume of the output gases from a pyrolysis facility is much less per tonne of feedstock processed than the volume from a combustion process [140] and this is a remarkable advantage since there is a significant minimisation of gas production [141]. Thus, all gas-containing components, especially the cleaning systems must be smaller than in incineration plants. Malkow [81] highlighted that both pyrolysis and gasification processes may reduce and avoid corrosive and hazardous emissions by retaining alkali and heavy metals within the process residues. Also dioxines and dibenzofuranes as well as thermal NOx formation are largely prevented due to the lower temperatures and the reduction conditions. In addition, it is remarkable that:

- Pyrolysis has the advantage of enabling the separation of most impurities such as sulphur from fuels prior to their combustion [70,142]. In WT pyrolysis, sulphur is principally retained as a char constituent (up to 70 wt% of the sulphur initially contained in tyre), whereas the liquid and gaseous products have relatively low sulphur contents and are suitable for low-sulphur emission fuel applications. In fact, up to 90 wt% of the sulphur contained in the tyre could remain in the solid and liquid fractions ($\sim$70 and 20 wt% respectively). Besides this, conventional temperature pyrolysis does not promote the separation of inorganic materials since hazardous ash components are not devolatilised [91], staying trapped in the solid fraction. For instance, Zn has a boiling point of 901 °C [60].
- PAHs generation is lower in comparison with direct tyre combustion when the volatile fraction released in the pyrolysis process is burnt. In WT pyrolysis, feedstock break in a solid and volatile fraction and this last one is free of solids that, as it is known, interact in the PAHs formation. According to Herlan [143], if any particular fuel has some PAHs, they could survive the further combustion process and settle on the soot as an unburned fuel fraction. Thus, if some fuel has a significant solid fraction, as WT (by the CB fraction) and this solid fraction is separated after its combustion, minor possibilities of PAHs generation could be achieved in comparison when the whole fuel is burnt.
- Due to the char produced in the pyrolysis process is mainly composed of CB, which has a fossil origin, the volatiles released in the pyrolysis process have a remarkable renewable content (up to 50 wt%) given NR incorporated in the tyre (Fig. 2). So, the use of the volatiles released in the WT pyrolysis produces lower fossil CO_2 emissions per unit of energy compared with the direct WT combustion and other conventional fossil fuels such as coal or fuel–oil, usually used in power generation as shown in Table 3 and reported by IEA [144]. This renewable content of the volatiles considered a 30 wt% of NR in the tyre and a 46 wt% of carbon according to a rubber woodchip elemental analysis [145]. The specific fossil CO_2 emissions for the volatile fraction released in tyre pyrolysis (136.51 gCO_2/kWh) represent differences of 167%, 159% and 48% for lignite, crude oil and natural gas respectively.
- If the pyrolytic CB produced has any commercial value, i.e. as raw material for the production of new rubber materials, electrically conductive agents in plastics, or as catalyst support in proton exchange membrane fuel cells, there will be a remarkable CO_2 emission reduction because there would be no new CB production and consequently CO_2 generation. The quantity of CO_2 per unit of CB produced depends on the type of process (acetylene black process, furnace black process, thermal black process) and ranging from 0.5 to 3.5 kg/kg [146]. The majority of the worldwide annual production is made through the furnace black process [147]. According to Rodat et al. [148] the furnace process gives about 5.7 kg CO_2 eq. per kg of CB produced. Tyres and rubber products represent the major end-use applications, accounting for about 90% of global CB market. In fact, most of the CB production facilities are located in countries that possess major tyre and automotive industries [147].

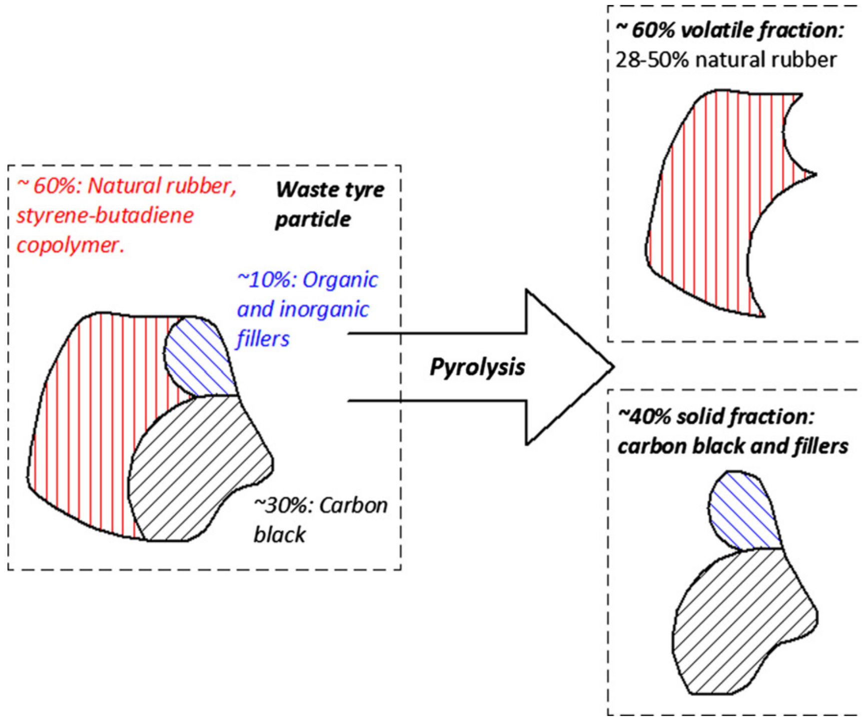


Fig. 2. Tyre pyrolysis scheme.

Table 3
CO_2 emissions from combustion of fossil fuels and volatiles released in WT pyrolysis.

Fuel	gCO_2/kW h	Times
Crude oil	353.76	2.59
Gas/Diesel oil	266.64	1.95
LPG	227.04	1.66
Anthracite	353.76	2.59
Coking coal	340.56	2.49
Sub-bituminous coal	345.84	2.53
Lignite	364.32	2.67
Peat	381.48	2.79
Natural gas	201.96	1.48
Volatiles released in WT pyrolysis	136.51	1.00

- No process emission from pyrolysis units, as pointed by Clark et al. [18]. Pyrolysis units are expected to have minimal air pollution impacts because most of the pyrolytic gas generated is burned as fuel in the process. The primary sources of emissions are fugitive sources (particulate emissions) and equipment leaks (VOCs emissions) around valve stems, pump shafts, worm packing and pipe joints. In addition, the absence or the low levels of oxygen present in the pyrolysis process helps inhibit the formation of dioxins and furans [140]. As stated by Roy et al. [149], no toxic substances are emitted and various commercial applications for all of the products obtained are possible.

Summarising, although pyrolysis of WT has been widely developed throughout the world [97], it is currently reduced to a limited scale and mainly for research purposes. One noteworthy problem consists of transferring the heat efficiently to drive the pyrolysis process in such a way that the temperature is evenly distributed. This is a remarkable bottle neck for industrial plants and this discourages its promotion and its economical and technical feasibility. Moreover, the products from tyre pyrolysis are more complex from the physical-chemical point of view than products from alternative thermochemical processes like combustion or gasification. This fact also causes that WT pyrolysis has not yet gained acceptance in industry as well-known process like combustion. Another important disadvantage is linked with legislative barriers because pyrolysis is classified as incineration in the EU. Any plant dedicated to the thermal treatment of wastes regardless the heat recovery is considered as incineration. Additionally, some authors [18,78,105,149–151] coincide that the absence of a wide market for the liquid and the solid fractions implies that WT pyrolysis is not widespread in industrial processes. Economical feasibly of WT pyrolysis process at large scale requires marketing of the products obtained. Murillo et al. [152] stated that although the pyrolysis process is technically and environmentally feasible, its economic viability clearly depends on the possible use of the three main derived products. The tyre liquid must compete with oil conventionally produced from crude at its current prices and this fact can be crucial for the pyrolysis economic feasibility given the current world energy panorama. Also, there is the problem of marketing the solid fraction as CB due to unfavourable characteristics concerning its high level of impurities (ash content). Pyrolytic CB contains as much as 10–15% ash, which adversely affects its reinforcing properties in new tyre manufacturing [18].

3. The governing variables in the tyre pyrolysis process

WT pyrolysis is an endothermic process that is maintained by temperature in the reactor. Therefore, temperature exerts a considerable effect in the products and conversion grade and for this reason, it is the governing variable with major influence on pyrolysis. The particle size, heating rate, pyrolysis time and volatiles residence time involved in the process also exert a remarkable effect. As it will be showed, particle size and heating rate interact in the heat transfer phenomena having a direct relation with the pyrolysis time, and consequently influencing the gas, liquid and solid distributions and their physicochemical

Table 4
Some investigations on WT pyrolysis.

Tyre's characteristics	System configuration	Operation parameters	Relevant results and observations	Ref.
Tyre shreds mixture of tyres from trucks, tractors and cars. Average particle size of 5 mm	AR designed to process 15 kg/h of WT. The tyre shreds move through the reactor and at the same time they decompose into a gaseous product and a solid residue	Temperature was varied at 600, 700 and 800 °C. N_2 as carrier gas at 11.4, 68.4 and 144 LN/h. Mass flow rate at 3.5, 6 and 8 kg/h. The range of the pyrolysis time was varied from 1.5 to 5 min	At 600 °C solid, liquid and gas fractions were of 40.6, 39.0 and 41.0 wt% respectively. At 800 °C they were 41.0, 27.5 and 31.5 wt%. Regardless the process operational parameters, a total WT devolatilisation was achieved, producing a pyrolytic CB with a volatile matter content under 5 wt%. The most influencing process variables were temperature and solid mass flow rate, mainly because both variables modify the volatiles residence time inside the reactor	[8]
Radial WT of different types and brands. Pieces of 25 × 30 mm^2 from the main tread area of the tyre, including the steel reinforcement	FBR. Cylindrical chamber (200 cm^3)	45 g of load. Heating rate of 10 °C/min. Temperature of 500 °C. Pyrolysis time of 60 min	60.1 wt% of liquid yield, 2.4 wt% of gas and 37.9 wt% of char for the tyres mixture. The yields of char, liquid and gas were very similar for the seven types of tyres investigated. Even so, the gas composition showed noticeable variations between the types. Also, some differences in the aromatic compounds were found in the liquid fraction	[16]
Shredded tyres into pieces of about 50 mm as well as fine particles	RKR with a capacity of 120 kg/h ($_{max}$. 250). The reactor was indirectly heated by oil and gas	Temperature varied between 540 and 750 °C	At 640 °C the liquid yield was around 50 wt%. At 600 °C the char fraction presented a high quality in terms of reuse as CB. It was obtained a heavy and a light oil fraction after quenching and condensing the volatiles released during the process. The uncondensable gas was partly returned to the process as purging gas and also used as a fuel for heating the kiln	[47]
A representative sample of the whole WT with all its components (steel belt. synthetic fabrics, etc.). Cross-section samples (2–3 cm wide)	FBR. Autoclave of 3500 cm^3	175 g of load. N_2 as carrier gas at 1 L/min. Heating rate of 15 °C/min. Pyrolysis time of 30 min. Temperature range between 300 and 700 °C	At 500 °C the liquid, gas and solid fractions were 38.0, 17.2 and 44.8 wt% respectively. Conversion grade did not change with temperature over 500 °C. The liquid characteristics did not present major differences for higher temperatures. This behaviour was attributed to the immediate extraction of the products generated	[50]
Pieces with different sizes: 2, 4, 8 and 12 cm^3 of MT. WT contained no steel cords but the textile fabrics	FBR fire-tube. The reactor height from the distributor to the gas exit was 270 mm and its diameter was 100 mm	N_2 as carrier gas at 8 L/min in order to guarantee an apparent vapour residence time of 5 s. Temperature range was from 375 to 575 °C	For feedstock sizes of 4 cm^3 the liquid yield at 475 °C was 49 wt%. The gas yield increased from 8 to 18 wt% over the temperature range. Char yield decreased as temperature was increased. The liquid fraction contained olefins, specially limonene and light aromatics. Density, viscosity, calorific value, carbon and hydrogen contents were found almost comparable to diesel fuels. However, a higher sulphur content and lower flash point were found	[51]
Shredded automotive tyres (2–5 cm^2 pieces) of light and heavy duty types including the metal core	FBR. 200 cm^3 static batch reactor	N_2 as carrier gas at 0.11 L/min. Temperature range between 300 and 720 °C. Heating rate range between 5 and 80 °C/min	At 600 °C and 40 °C/min were obtained 54.8 wt% of liquid, 12.0 wt% of gas and 33.2 wt% of char. As the pyrolysis temperature was increased the char yield decreased, whilst gas and liquid yields increased until 720 °C. The gas evolution was dependent on temperature and heating rate	[52]
Shredded PCT with both steel and fabric cords. 3 cm wide 1.5 cm thick and of between 50 and 150 cm maximum dimension	Large-scale FBR. 24 cm of inner diameter and 36 cm of height	3 kg of load. Temperature range between 450 and 600 °C. Heating rate of 5 °C/min N_2 as carrier gas. Pyrolysis time of 90 min	At 525 °C was produced 56.9 wt% of liquid, 37.8 wt% of char and 5.2 wt% of gas yield. Results were corrected for the percentage mass of steel core. The char yield remained fairly constant from 450 to 600 °C. The liquid yield was found to decrease with increasing temperature and the gas yield increased	[54]
WT samples with two particle sizes of 0.32 mm and 0.8 mm	CFBR with a processing capacity of 5 kg/h. Internal diameter of 100 mm and a total height of 2.9 m. Sand quartz as inert material. The system was operated under a slight vacuum	Heating rate could reach about 103 °C/s and the volatiles residence time was around 1–5 s. Part of the pyrolysis gas was used as the carrier gas	From 360 to 810 °C the gas yield increased from 10 to 40 wt% whereas the char yield decreased up to 27 wt% at 450 °C and then remained almost constant. The liquid fraction increased first to a maximum value of about	[55]

Table 4 (*continued*)

Tyre's characteristics	System configuration	Operation parameters	Relevant results and observations	Ref.
			50 wt% at 450 °C. and then decreased. The liquid fraction was composed of aromatics, alkanes and asphalt compounds. CH_4 and H_2 increased with temperature. As the volatiles residence time increased from 1 to 5 s, the liquid and char decreased whilst the gas increased slightly	
Shredded automobile tyres (0.2–1.6 mm of diameter particle size) including the metal core	FBR. A cylindrical stainless-steel atmospheric pressure reactor	N_2 as carrier gas at 75 cm^3/min. Temperature range between 350 and 700 °C. Heating rate between 5 and 20 °C/min. Pyrolysis time of 30 min	Between 450 and 575 °C, the char yield was between 37 and 40 wt%, the liquid fraction remained around 55 wt% and the gas fraction was between 4 and 11 wt%. The solid fraction showed a higher calorific value of 28 MJ/kg. Char yield decreased and gas yield increased with increasing temperature. Increasing the heating rate led to similar results to those obtained with temperature	[56]
Shredded scrap tyres with particle size of 13–15 mm including the fabric cords but not the steel	Continuous RKR electrically heated. The feeding rate can be regulated from 10 to 30 kg/h. Diameter 30 cm and overall length 3 m	Temperature range between 450 and 650 °C. Pressure (negative) between −10 and −20 Pa. Feeding rate between 12 and 15 kg/h	As the reactor temperature increased, the char yield remained constant around 40 wt%. The maximum liquid yield was 45.1 wt% at 500 °C. The pyrolytic derived liquids could be used as liquid fuels given their high calorific value (40–42 MJ/kg), reasonable viscosity (1.6–3.7 cS) and sulphur content (0.97–1.54 wt%)	[58]
Chinese PCT. Granulates in a size range of 20–60 mesh	FBR. Inner diameter of 32 mm and 120 mm of height. Several stainless steel plates were fixed in the reactor to strengthen heat transfer	100 g of tyre granules mixed with 3.0 g of NaOH were loaded in the reactor. The process was carried out under vacuum pressure (3.5–10.0 kPa). Temperature range between 450 and 600 °C	The maximum liquid fraction yield was 49.7 wt% at 480 °C, later this fraction decreased with increasing pyrolysis temperature. NaOH played an important role in the pyrolysis of WT since the process could be conducted at lower temperature. The pyrolysis liquids were distilled under atmospheric pressure up to 205 °C to separate the naphtha fraction from the pyrolytic liquid	[62]
Tyres powder with particle size between 200 and 400 μm	FBR. 10 mm diameter and 50 mm of height	N_2 as carrier gas at 0.56 m/s of superficial velocity. Temperature ranging from 400 up to 600 °C. Heating rate of 300 °C/min. Pyrolysis time of 15 min	At 500 °C, liquid and solid yields were around 43 and 38 wt% respectively. The pyrolysis reaction started at 200 °C and finished between 480 and 490 °C. No influence of the reaction time and heating rate on the total conversion and liquid yield was observed in the range studied.	[63]
PCT. Particles around 2 mm	FBR heated electrically. Internal diameter of 60 mm and 140 mm height	10 g of load. Heating rate of 10 °C/min. N_2 as carrier gas at 100 mL/min. Pyrolysis time of 1 h. Temperature from 375 °C to 500 °C	The maximum liquid yield (60 wtwt%) was achieved at 425 °C. Solid yield decreases up to 26 wt% at 450 °C and then remained almost constant. The liquid fraction consisted of 79.77 wt% of *n*-pentane soluble (mantenes) and 20.23 wt% of asphaltenes. The fuel properties of the liquid fractions such as H/C ratio, density, viscosity, calorific value and elemental composition were similar to those of conventional fuels	[65]
Powder tyres with 600 μm of particle size	FBR. A stainless steel reactor of 40 mm diameter and 90 mm of height	3.5 g of load. CO_2 as carrier gas varied between 50 and 150 mL/min. Temperature range between 800 and 900 °C. Pyrolysis time varied between 60, 90, 120, 150 and 180 min	At 900 °C, 150 mL/min of CO_2 and 180 min of pyrolysis time, the liquid, gas and solid fraction were 48.5, 26.0 and 25.6 wt% respectively. Surface area of the solid fraction was around 414 m^2/g. It was confirmed that there were two consecutive stages (devolatilisation and activation) in the same process. A temperature higher than 760 °C, the CO_2 started to oxidize the remaining CB	[67]
Tyre material (free of metal reinforcing) ground mechanically to pass through a 420 mm screen	Horizontal oven where it was located a quartz tube reactor of 40 cm long and 7 cm in diameter	50 g of load. He as carrier gas at 200 mL/min. Pyrolysis time of 1 h. Temperature was varied at 350. 450 and 550 °C	At 350 °C, solid, liquid and gas fractions were 50, 30 and 20 wt% respectively. At 450 °C, they were 40, 33 and 27 wt%, and at 550 °C were 33, 38 and 29 wt%. The solid residue showed a carbon content of around 80 wt%. Sulphur and chorine initially in the tyre was concentrated in the solid fraction. The liquid fraction	[68]

Table 4 (*continued*)

Tyre's characteristics	System configuration	Operation parameters	Relevant results and observations	Ref.
			showed a high calorific value around 40 MJ/kg	
Shredded TT fed 21 and 42 kg/h	A semi-continuous pilot plant of 3 m of long and 60 cm of diameter. Commercial eutectic molten salts circulated counter-currently with the feedstock	Temperature range of 431–471 °C (at different locations of the reactor inside wall). Total pressure of 12 kPa. Feed rate of 33 kg/h	Liquid yield of 53.7 wt%. gas yield of 7.0 wt% and char yield of 39.3 wt%. The naphtha and D,L-limonene were around 23.7 and 3.6 wt% respectively. The pyrolysis vapours were evacuated from the reactor by means of a vacuum pump. The vapours were condensed in two packed towers indirectly cooled with tap water	[78]
Granulated scrap tyres	BFBR at laboratory scale (0.1 kg/h). Diameter of 5 cm and a fluidising zone of up to 8 cm	500 L/h of either N_2 or circulated pyrolytic gas. Temperature range between 640 and 840 °C	At 640 °C the char yield was around 40 wt% and increased as the temperature was increased. By increasing the temperature, the yield of H_2, CH_4 and C_6H_6 increased and the liquid yield decreased. The liquid fraction presented a high aromatic content	[102]
Pieces of scrap tyres up to a weight of 2.7 kg/each. Also individual unshredded tyres (20 kg) can be processed	BFBR with internal dimensions of 90 × 90 cm for processing 1.5–2.5 t/d of scrap tyres	A sand bed or CB bed was indirectly heated between 650 and 850 °C by seven radiating fire-tubes. Also a fraction of the pyrolysis gas was burnt and also acted as a fluidising medium	At 720 °C, the principal products were 22 wt% gas, 27 wt% liquids, 39 wt% char and 12 wt% steel cord. A rich gas of CH_4 and C_2H_4 as well as a liquid fraction with a high percentage of aromatic compounds were produced. It was proved the feasibility of whole-tyres pyrolysis. After 2 or 3 min, the tyre was completely pyrolysed	
Scrap tyres	FBR (counter-current) with 100 mm of internal diameter. WT was fed continuously and the solid fraction was removed by means of a rotary grate	Temperature range of 400–700 °C. Carrier gas N_2 and CO_2	In the temperature range studied 36–38% of char, 49–38% of liquid and 15–30% of gas were obtained. Char showed a surface area around 570 m^2/g when CO_2 was used as carrier gas. Pyrolysis products were rapidly removed and at the same time char was activated. The H/C ratio of the liquids was about 1.5. The char yield remained constant whilst the liquid yield decreased with the temperature due to a greater degree of cracking	[104]
Shredded tyres between 6.35 and 12.70 mm with no steel belt	Bench scale reactor (1 kg of feedstock)	Temperature range up to 500 °C. Pressure was maintained below 3 kPa abs.	The maximum yield of liquid (60.7 wt%) was reached at 415 °C. The gas fraction had a gross calorific value of 37 MJ/kg. From the bench scale reactor, two systems operated on a semi-continuous feed mode (13 kg/h) and also a continuous pilot plant with 200 kg/h of capacity were scale up	[111]
Scrap tyres with a particle size lower than 2 cm.	A pilot scale RKR externally heated (110 dm^3 in volume and 0.4 m in diameter), working with a light over-pressure (as maximum 300 mm w.c.)	Temperature between 550 and 680 °C. The feeding rate was fixed at 4.8 kg/h. N_2 as carrier gas at 1.4 m^3/h. Rotating speed of 3 rpm	At 550 °C the char, liquid and gas production were 49.09, 38.12 and 2.39 wt% respectively. Temperature did not influence seriously the volatilisation reaction yield at least from a quantitative point of view, while the distribution of the volatile fraction (liquid and gas) and its properties showed some influence	[138]
Sidewall rubber of WT (1 cm diameter, 3 mm thickness)	FBR. A reactor glass tube (diameter 30 mm, length 500 mm) heated by an electric furnace	N_2 as carrier gas at 0.2 L/min. Temperature range 380–550 °C. The pyrolysis time was around 15 min	At 550 °C, the liquid. gas and char yield were 12. 53 and 35 wt% respectively. H_2 and CH_4 increased with temperature and this behaviour was attributed to dehydrogenation reactions and structural arrangements of gaseous and liquid hydrocarbons	[153]
Powder tyres free of steel with particle size less than 500 mm	Captive sample reactor at atmospheric pressure with an inner diameter of 7 cm and 12 cm of height	200 mg of load. He as carrier gas at 30 cm^3/min. Heating rate between 70 and 90 °C/s. Temperature ranging from 390 to 890 °C	Char yield decreased with temperature reaching an asymptotic value of 20 wt% at 830 °C. Gas yield increased with temperature reaching an asymptotic value of 73 wt% also at 830 °C. Once the pyrolysis process was conducted, the char was gasified with steam and CO_2 producing activated carbons with surface areas comparable with those of commercially available active carbons	[154]
Shredded tyres with a mean diameter of 5 mm.	BFBR. Internal diameter of 6.9 cm and 43.2 cm of height. Sand of 0.105–	Temperature ranged from 600 to 900 °C. He as carrier gas	The yield of total gas increased in the range between 600 and 800 °C from	[155]

Table 4 (*continued*)

Tyre's characteristics	System configuration	Operation parameters	Relevant results and observations	Ref.
	0.210 mm of particle size was used as inert material		6.3 to 37.1 wt%. The solid fraction also increased as temperature increased. The formation of CH_4. H_2. C_6H_6 and C_7H_8 were favoured by longer residence times. Heavier hydrocarbons were cracked at increasing residence times and/or temperature	
Scrap tyres. Pieces of 20 mm × 20 mm including the metallic grid and the textile part	FBR. A stainless steel reactor of 5.5 cm diameter and 40 cm of height	300 g of load. Heating rate around 12 °C/min. N_2 as carrier gas at 0.4 L/min. 4 h of pyrolysis time. Residence time of the volatiles: 1–1.5 min. Temperature varied from 400 to 700 °C	In the temperature range studied global yields were 64–51 wt% for solids (carbonaceous residue and steel), 30–43 wt% for the liquid fraction and 2.4–4.4 wt% for the gas fraction. The minimum pyrolysis temperature was 450 °C. From this temperature, the yield to char was basically constant. The composition of the gas fraction was highly dependent on temperature. High temperatures promoted cracking of the heaviest compounds	[156]
Cuboids of automotive WT. Dimensions 45.2 × 2 × 4 mm	Quartz tube reactor of 10 mm internal diameter	1 g of load. He as carrier gas at 0.67 mL/s in order to prevent backward flow of the water steam. Steam flow rate varied between 0 and of 1.5 mg of water/s per gram of sample. Temperature varied between 700 and 900 °C	At 0.75 mg of water/s per gram of sample, 900 °C and 60 min of reaction time, the char yield was 9 wt% and the surface area was 1260 m^2/g. H_2 and CO were the prime components of the gaseous fraction and aliphatic hydrocarbons and akylbenzenes were the major components of the liquid fraction. Also, the char yield decreased as steam was feed and temperature increased	[157]
Particle size lower than 1 mm. The feedstock was free of steel and other tyre carcass elements	CSBR. The total height of the reactor was 34 cm and the height of the conical section was 20.5 cm. The diameter of the cylindrical section was 12.3 cm	Temperature range 425–600 °C. A bed of 35 g of sand (particle diameter 0.63–1 mm) was used to guarantee a good heat transfer and isothermicity. The carrier gas was N_2 at 9.5 L_N/min	In the whole temperature range, it was obtained 1.8–6.8 wt% of gases. 44.5–55.0 wt% of liquid fraction (C_5–C_{10} range hydrocarbons), 9.2–11.5 wt% of tar (C_{+11}) and 33.9–35.8 wt% of char. Results were compared with pyrolysis in batch mode. The main difference was in the yield of light aromatic compounds which was higher in the continuous process, whereas the heavy liquid fraction was higher in the batch process	[158]
Tyre shreds with a particle size between 1 and 5 cm	RKR working in batch mode	20 kg of tyre processed per batch. Temperature between 500 and 600 °C. By means of a suction pump. the gaseous products were rapidly removed. The process lasted about 30 min	The solid and gas fractions were 33–34 wt% and 67–66 wt% respectively. The lower calorific value of the gas fraction was around 33 MJ/m^3. Only two fractions were produced (solid and gas) given the operation conditions (long pyrolysis time and steep heating ramp), which minimise the possibility of obtaining a liquid fraction	[159]
Two samples of tyre powder: 200 and 600 μm of average particle size	Radio-frequency (RF) plasma reactor operated between 1600 and 2000 W. The plasma reactor is a quartz tube with an inner diameter of 16 mm and a length of 500 mm	The reactor pressure was varied between 3000 and 8000 Pa (absolute pressure). The reactive plasma environment has a gas (N_2) temperature between 927 and 1527 °C. The sample was fed into the plasma reactor at 0.2–0.5 g/min	Increasing the RF power from 1600 W to 2000 W, the solid conversion increased from 40 to 76.8 wt%, and the H_2 increased from 38.6 to 44.4vol%. Similar results were found when pressure was increased. Plasma pyrolysis of waste rubber gave only two product streams: combustible gas and pyrolytic CB. The major components of the gas product were H_2, CO, CH_4. and CO_2. The solid fraction showed a particle size about 50 nm	[160]

properties. Also, the carrier gas flow and the atmosphere type have also an important effect in the process, controlling the occurrence of secondary pyrolysis reactions such as thermal cracking, repolimerisation, recondensation and/or char formation.

This section shows an exhaustive survey regarding the effect of temperature, pressure, feedstock composition, particle size, heating rate, carrier gas flow rate and type, pyrolysis time and residence time of the volatiles on the liquid, gas and solid yields as well as their physicochemical properties. All reported results have been framed regarding the type of reactor used in order to avoid contradictions among the large number of publications related with WT pyrolysis. Secondary reactions seem to be very sensitive to the governing variables and differences among results are ascribed to their occurrence. Likewise, as a general overview, Table 4 shows an extensive review of different results and remarkable observations on WT pyrolysis conducted under different technologies and process conditions. This table also serves as guide for the identification of the pyrolysis conditions applied by the several authors cited along this paper, helping with the comparison among results.

3.1. Feedstock composition

The exact composition of tyres depends on brand, age and type [15,16,51,161] and this composition and the processing method may often be held secret by the different tyre producers [64]. Consequently, the yield and physicochemical properties of the pyrolysis products also vary. Depending on the category (TT, PCT, MT), different contents of NR and SR can be found in the tyre. As reported in the literature associated [1,69,162] TT has higher NR content than PCT as shown in Table 5 [162]. The ratio of natural to synthetic rubber is approximately two to one in TT and four to three in PCT [3].

Although it is generally assumed that rubber degradation begins to be appreciable around 200 °C and above this temperature significant yields of volatiles are released [77,63,156], the exact degradation behaviour of the tyre depends on the contents and distributions of the rubber compounds (NR, SBR and BR). For instance, Kwon and Castaldi [79] reported a rate of thermal degradation of 0.25 and 0.21 wt%/s for both SBR and polyisoprene rubber respectively, and these values were higher than the tyre sample used (0.5 wt%/s). Additionally, temperature decomposition range of tyre (280–500 °C) was wider than that for polyisoprene and SBR both between 320 and 480 °C. Many works about the thermal degradation behaviour of these compounds are found in literature although some differences can also be noticed. Differences are ascribed to intrinsic phenomena associated with the TG apparatus and technique, the conditions implemented (higher heating rates shift thermal degradation to higher temperatures) and also some possible variances in the tyre compounds (processing oil). Even so, all results agree regarding the temperature range where the main tyre compounds are degradated. Generally speaking, it is possible to say that NR decomposes first (~380 °C), followed by SBR (~450 °C) and BR (~460 °C). Table 6 shows characteristic degradation temperatures for NR, SBR and BR reported in literature.

Similarly, many results have been reported along the wide literature on WT pyrolysis about the differences in properties and yields of different types of tyres. For instance, Cypres and Bettens [97] showed significant variations, of the order of 10%, in the yields of solid, liquid and gaseous products after pyrolysing different brands of tyres. Likewise, Zhang et al. [62] emphasised that the different characteristics of the tyre can contribute to the different contents of naphtha in the pyrolytic liquid. Similarly, Kyari et al. [16] found noticeable variations in the gas composition for seven different PCT brands pyrolysed in a FBR under identical conditions. The gross calorific value of the gases showed values between 29.9 MJ/m^3 and 42.1 MJ/m^3. Variations in the concentration of certain aromatic compounds in the pyrolytic liquids were also obtained, although very similar yields of char, liquid and gas were found.

Ucar et al. [69], besides to report different liquid yields for PCT and TT (47.4 and 55.6 wt% respectively) at 550 °C, showed remarkable differences in the aromatic content and also in the sulphur content of these two liquids. For PCT those contents were 41.54 vol% and 1.35 wt% respectively, whereas for TT they were 15.41 vol% and 0.83 wt% respectively. The difference in the aromatic content was mainly ascribed to the feedstock composition. NR content in TT was higher (51 wt%) than PCT (35 wt%). Similar conclusions were reported by Buekens [25] for the liquid obtained from TT pyrolysis. The lower aromatic content was attributed to the higher NR content in the WT. Moreover, the pyrolytic CB derived from TT was found more suitable for the production of activated carbon due to its lower ash content (14.3 wt%) in comparison to PCT (40.3 wt%). According to Roy et al. [165] tyre pyrolysis produces more aromatic compounds than the pyrolysis of pure polyisoprene (NR). They ascribed this behaviour to the aromatic nature of the rubber feedstock given the presence of SBR and the processing oil used in the tyre manufacture. Similarly, Kwon and Castaldi [166] suggested that the first reactions during the thermal breakdown of SBR are aromatic radical species. Likewise, Islam et al. [51] reported a lower aromatic (16.65 wt%) and higher aliphatic (49.54 wt%) concentrations in the pyrolytic liquid obtained at 475 °C from MT. The aliphatic compounds were mainly of alkane and alkene groups being predominant the non-saturate fraction (43.23 wt%). The authors related this behaviour to the presence of SR in the MT as well as some possible ciclisation and dehydrogenation reactions. The influence of tyre composition on the pyrolysis process was also showed by López et al. [167] using a CSBR. Among other characteristics, the yield to aromatics was lower in the tyre type commonly used for manufacturing TT (33.4 wt%) than the tyre type with typical formulation used for PCT (43.7 wt%) at 500 °C. The contents of NR and SBR were 58.9 and 0 wt% respectively for the former tyre type and both 29.6 wt% for the latter one. The authors, in accordance with the results showed before, suggested that the SBR degradation gives way to a higher amount of aromatic hydrocarbons. Table 7 summarises the results discussed above.

Table 5
Chemical composition of tyres [162].

Compound	Passenger car tyre (wt%)	Truck tyre (wt%)
Natural rubber	14	27
Synthetic rubber	27	14
Carbon black	28	28
Steel	14–15	14–15
Fabric, fillers, accelerators, antiozonants, etc.	16–17	16–17

3.2. Temperature

3.2.1. The temperature effect on the pyrolysis yields

As previously stated, the main variable affecting tyre pyrolysis is temperature [8,12,50,56,63,68,139]. From the conversion point of view and according to several authors [12,50,63,69,156,168,169] 500 °C appears to be the optimum temperature, at atmospheric pressure, since total tyre conversion is achieved. At lower temperatures, the main tyre compounds (SBR, BR and NR) still remain in the pyrolytic CB, showing a heterogeneous

Table 6
Temperature for degradation of the main tyre compounds reported in literature.

NR			SBR			BR			Heating rate (°C/min)	Ref.
Initial	Peak	Final	Initial	Peak	Final	Initial	Peak	Final		
325	375	460	350	455	485	405	455	485	5	[15]
300	377	475	300	444	490	340	465	500	10	[91]
300	365	470	300	447	480	300	465	500	10	[163]
280	378	460	300	458	500	340	468	510	10	[164]

Table 7
Feedstock composition effect on tyre liquid.

Tyre type	NR content (wt%)	SR content (wt%)		Aromatics (wt%)	Aliphatics (wt%)	Pyrolysis temperature (°C)	Reactor type	Ref.
		SBR	BR					
MT	n.r.	n.r.	n.r.	16.65	49.54	475	FBR	[51]
PCT	35	65	0	41.54[a]	3.91[a,b]	550	FBR	[69]
TT	51	39	10	15.41[a]	20.47[a,b]			
PCT	29.6	29.6	n.r.	43.7	n.r.	500	CSBR	[167]
TT	58.9	0	n.r.	33.4	n.r.			

n.r., not reported.
[a] vol%.
[b] Olefins.

Table 8
Pyrolysis product yields reported in literature without remarkable effect of temperature.

Average product yields (wt%)			Temperature range (°C)	Type of reactor	Experimental conditions	Ref.
Gas	Liquid	Solid				
17.5[a]	38.3[a]	44.2[a]	From 500 to 700	FBR	A piece of tyre of 2–3 cm (wide) pyrolysed under N_2 at 1000 cm^3/min and 15 °C/min	[50]
6.0	61.0[c]	33.0	From 415 to 500	Bench scale reactor	Pyrolysis under vacuum pressure, below 3 kPa	[59]
7.6[a] 8.0[b]	50.7[a,c] 58.4[b,c]	41.7[a] 33.6[b]	From 550 to 800	FBR	130 g of scrap tyres pyrolyzed at 7 °C/min up to the desired temperature and hold for 1 h	[69]
6.8[d]	53.1	40.1	From 500 to 1000	RKR[e]	Particle size < 0.42 mm. The sample (200 g) was heated at 5 °C/min up to desire temperature at 500 mL/min of N_2	[168]

[a] Passenger car tyre.
[b] Truck tyre.
[c] Taking into account the water content.
[d] Obtained by difference.
[e] Laboratory-scale rotary furnace.

sticky-gummy aspect, as highlighted by Rodríguez et al. [50]. In this sense, TG studies give an important operational window for each variety of tyre as well as the process conditions such as flow and type of carrier gas, and heating rate among others.

Even though temperature is the main governing variable on tyre pyrolysis, the final effect is accompanied by other variables involved in the process such as pressure, heating rate and superficial velocity of the carrier gas. All these variables play an important role in the occurrence of secondary reactions. A strict pyrolysis process without secondary reactions should not show major variations in the product yields as the temperature increases. This performance is ensured at higher flow rates of carrier gas or performing the process under vacuum pressure. Table 8 shows the average pyrolysis product yields reported by different authors using different experimental systems. No major variations on the product yields were reported in the temperature range.

On the other hand, an increase in the temperature could promote an increase in the gas fraction yield at expenses of the liquid fraction yield. However, as commented above, this is conditioned by the occurrence of secondary reactions. For instance, Chang [53] reported a thermal cracking effect of the liquid fraction when the process temperature was increased. This study was performed in a TG balance under N_2 atmosphere (50 cm^3/min) using particle size around 2 mm. The author found a gas yield above 50 wt% at 550 °C and a very slightly decrease of the solid fraction when temperature increased from 350 to 550 °C. Similarly, Kawakami et al. [47] using a RKR found a decrease in the liquid yield and an increase in the gas yield when temperature increased from 540 to 740 °C. Only a slight difference was found in the char yield decreasing from 38 and 40 wt% in the temperature range. Despite this, the authors highlighted that the char properties regarding its further use can be altered over the temperature range studied. More examples are shown in Table 9, where it is possible to find the temperature effect on pyrolysis product yields reported by different authors using different reactors and experimental conditions.

Moreover, solid fraction can also increase as the pyrolysis temperature increases. This behaviour usually occurs in fluidised bed and spouted bed reactors or in processes at very high temperature where tar and char formation are favoured. In this type of reactors the higher heating rates and the vigorous gas–solid contact can promote additional secondary reactions involving the solid pyrolytic CB particle [102,155,170,171]. Thus, the volatile products released in the pyrolysis process can be absorbed on the surface of char giving way to new carbonaceous materials. Under this context, more gas and pyrolytic CB and less liquid is expected when the temperatures increases. For instance, Conesa et al. [155] using a BFBR reported an increase in the solid fraction at higher temperatures, passing from 20.4 wt% at 600 °C to 32.5 wt% at 900 °C. In a conical spouted bed reactor (CSBR), López et al. [171] found that the higher the temperature, the higher the deposition of heavy hydrocarbons on the surface of the solid fraction, leading to an increase in the mass obtained. The solid fraction yield increased from 33.9 to 35.8 wt% at 425 and 600 °C respectively. In another work, Conesa et al. [60] using a FBR did not find liquid fraction generation at 1000 °C but a higher solid fraction composed of pyrolytic CB (~37 wt%) and a carbonaceous solid (~25 wt%).

As a final conclusion, albeit temperature is the main governing variable in pyrolysis, its final effect is also influenced by the specific characteristics of the system such as heating rate, type of carrier gas and flow rate and pressure, which have a direct influence in the promotion of secondary reactions and

Table 9
Temperature effect on pyrolysis product yields reported in literature.

Average product yields (wt%)			Temperature (°C)	Type of reactor	Experimental conditions and observations	Ref.
Gas	Liquid	Solid				
17.9	41.5	40.6	600	AR	Mixture of tyres from trucks, tractors and passenger cars with a particle size around 5 mm. N_2 flow of 11.4 L_N/h	[8]
29.7	31.3	39.0	700			
31.5	27.5	41.0	800			
9.0	47.0	44.0	425	FBR	Motorcycle tyres of 4 cm^3. The volatiles residence time was around 5 s (8 L/min of N_2)	[51]
10.0	49.0	41.0	475			
19.0	41.0	40.0	575			
4.5	58.1	37.4	450	FBR[b]	Passenger car tyres as feedstock pyrolysed at 5 °C/min. The maximum residence time in the reactor was around 120 s	[54]
5.2	56.9	37.8	525			
8.9	53.1	38.0	600			
6.0	55.4	38.6	500	FBR	4 g of scrap tyres (passenger car tyre) were pyrolysed at 75 cm^3/min	[56]
10.8	52.2	37.0	600			
26.7	36.6	36.7	700			
14.0	46.0	38.0	500	FBR[a]	N_2 as a carrier gas. Similar trend using CO_2	[104]
18.0	43.0	38.0	600			
22.0	38.0	38.0	700			
2.4	38.1	49.1	550	RKR	Pilot plant working with a light over-pressure (maximum working pressure of 300 mm w.c.); 4.8 kg/h of feeding rate and 1.4 m^3/h of N_2	[138]
8.2	33.0	47.4	600			
10.7	31.8	48.9	680			

[a] Continuous counter-current reactor.
[b] Large-scale FBR.

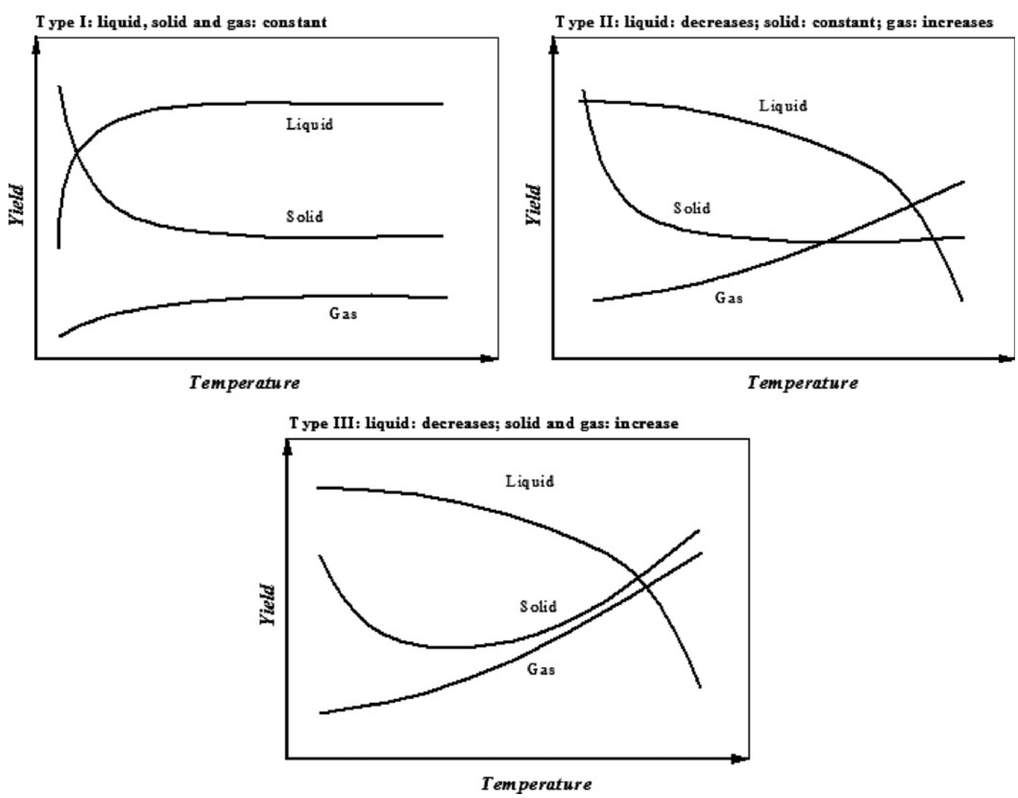


Fig. 3. Yields of tyre pyrolysis products at different conditions.

consequently in different yields of liquids, gas and pyrolytic CB. Fig. 3 shows different behaviours of the pyrolysis yields as a function of temperature. Type I represents the normal behaviour of pyrolysis without secondary reactions. In a strict sense, there are only primary pyrolysis products which result from the breakage of bonds followed by some molecular or free radical rearrangement. Type II stands for a pyrolysis process where secondary reactions involve both liquid and gas fractions whilst solid fraction remains constant. Gas fraction increases at expense of the liquid one. Type III corresponds to an usual behaviour for processes with vigorous gas–solid contact that encourage secondary reactions increasing both the solid and the gas fraction yield.

3.2.1.1. The temperature effect on the liquid fraction. Generally speaking, for plastic feedstock pyrolysis as it is the rubber contained in WTs, the properties of the liquid fraction can change with temperature, usually containing larger quantities of aliphatic compounds at lower temperatures than at higher temperatures where aromatic production is promoted [74]. However, it is worth noting that the increase of aromatic compounds is conditioned by

secondary reactions that modify the chemical properties and yields of the products as shown before (pyrolysis behaviour Type II and III). Williams' works [4,54] have showed a remarkable influence of the temperature regarding the aromatic and aliphatic compounds in the liquid fraction obtained from WT pyrolysis. For example, it was found an increase in the aromatic content and a consequent decrease in aliphatic content when temperature increased from 450 to 600 °C using a FBR [54]. In addition, the gross calorific value decreased slightly from 42.6 to 41.2 MJ/kg. In the same way, Li et al. [58] found the same tendency using a pilot-scale RKR. As the temperature was increased from 450 to 600 °C, the H/C ratio decreased from 1.55 to 1.26 indicating more aromatic compounds. BTX compounds also showed a notably increase. The calorific value slightly decreased from 41.9 to 41.0 MJ/kg in the whole temperature studied. Kaminsky et al. [170] reported that the liquid fraction obtained at 600 °C in an indirect heated BFBR contained mainly aliphatic species whilst more aromatics were found at 700 °C. Likewise, Aylón et al. [8] using an AR observed that the aromatic compounds increased as the temperature increased from 600 to 800 °C. The authors also revealed that the yield of the lowest boiling point fraction obtained by simulated distillation of the tyre liquid increased notably (from 46% to 59%) as temperature increased. According to Benallal et al. [114] high pyrolysis temperatures favour the formation of conjugated bonds in the tyre liquid, and consequently, improve its properties as a refining feedstock and for the production of an octane booster. In contrast, olefinic and diolefinic hydrocarbons (predominant at lower temperatures) are undesirable compounds in gasoline, owing to their greater oxidation and polymerisation tendencies. These reactions could lead to the formation of gums that could damage engine fuel delivery systems.

3.2.1.2. The temperature effect on the gas fraction. Gas compounds and yield are very sensitive to secondary reactions such as thermal cracking as well as heterogeneous reactions involving the inorganic compounds of tyre. For this reason, the gas fraction behaviour in terms of composition, calorific value and yield is still quite disparate among all results reported in literature. For instance, Díez et al. [68] ran experiments in a quartz reactor placed in a horizontal oven at 5–60 °C/min and showed that the gas stream was more enriched with CO, CH_4 and H_2 whilst C_2H_6, C_3H_6, C_4H_6, the remaining C_4 hydrocarbons and C_5 and C_6 compounds as well as CO_2, decreased as the temperature increased (from 350 to 550 °C). The calorific value also decreased as the temperature increased (from 50 to 36 MJ/m^3) since the concentrations of heavier hydrocarbons decreased. Simultaneously, the gas yield increased from 20 to 29 wt% as consequence of cracking reactions. Napoli et al. [153] also monitored the gas evolution regarding its composition and production when WT pyrolysis was carried out in a FBR under N_2 atmosphere at three different temperatures: 380, 450 and 550 °C. At 380 °C the gas was constituted by small quantities of CO_2 and CH_4 and the total gas volume did not exceed 0.5 N m^3/kg. At 450 °C the total gas volume reached 3 N m^3/kg. CO_2 appeared at the beginning of pyrolysis and remained the major constituent in the following fractions. At 550 °C the total gas volume evolved was about 4.5 N m^3/kg and its half part was constituted mostly by CH_4 and H_2. A similar trend was reported by Conesa et al. [60] using a FBR pilot plant. From 450 to 1000 °C there was a considerable increase of CH_4 and C_6H_6 as well as H_2 as consequence of cracking reactions. Galvagno et al. [138] using a RKR also found an increase in both the total gas production and the calorific value (from 22 to 29 MJ/m^3) when the temperature increased from 550 to 680 °C. The authors highlighted the prevalence of secondary reactions on both the cyclisation and the hydroaromatic reactions (with a significant CH_4, C_2 and C_3 increase in comparison with the H_2). González et al. [56] observed an increase of both gas fraction yield and COx ($CO+CO_2$) yield as temperature increased from 400 to 700 °C. The authors attributed this behaviour to the decarbonilation and decarboxilation reactions and pyrolytic CB secondary reactions. An increase of both temperature (from 400 to 700 °C) and heating rate (from 5 to 20 °C/min) increased the concentration of CH_4, C_2H_4 and C_2H_6 with the concomitant increase in the calorific value (from 12 to 43 MJ/m^3, and from 20 to 29 MJ/m^3 respectively). Berrueco et al. [156] found that temperature had higher influence on the gas composition than on the yields of the different fractions. They used a FBR at 12 °C/min and a N_2 flowrate of 0.4 l/min leading volatiles residence times between 1 and 1.5 min. The authors reported that the COx fraction showed an initial maximum value of 0.55 wt% at 400 °C, which decreased slightly between 400 and 550 °C and increased slightly at further higher temperatures. H_2 showed a maximum production at 550 °C suggesting an increase as the temperature was increased. The calorific value increased as temperature increased (ranging from 5.5 to 9.0 MJ/Nm^3) but was remarkably lower in comparison to other works.

A similar tendency regarding cracking reactions occurrence is also found in fluidised bed reactors where these secondary reactions prevail noteworthy. Kaminsky and Sinn [102] reported an increase in CH_4, H_2 and C_6H_6 as the temperature increased from 640 to 840 °C. Also, using a BFBR Conesa et al. [155] stated that the gas yield increased from 6.3 to 37.1 wt% when temperature increased from 600 to 800 °C. At 800 °C CH_4 and C_2H_4 were the major components on the gas fraction. Both compositions were around 6.1 wt%. Similarly, in a continuous CSBR, López et al. [158] observed an increase in C_1–C_4 gas fraction as temperature increased from 425 to 600 °C. Gas yield increased from 1.81 to 8.26 wt% as a result of more severe thermal cracking at high temperatures. The gases were mainly composed of CH_4 and C_2–C_4 olefins.

Therefore, the temperature effect on the gas fraction mainly depends on the appearance of secondary reactions. Temperature is the key variable for increasing the gas fraction yield (pyrolysis behaviour Type II and III) since these secondary reactions, specially thermal cracking, are very sensitive to the temperature increase. It is expected that longer chain hydrocarbons decrease as temperature increases in favour of lighter hydrocarbons and H_2.

3.2.1.3. The temperature effect on the solid fraction. From a strict pyrolysis point of view, no major changes on the solid fraction yield are expected when pyrolysis temperature increases (pyrolysis behaviour Type I and II). Hence, the amount of the solid fraction must be similar to the sum of the original CB and the ash content. However, as shown before, the solid fraction can be higher than this expected value due to the occurrence of secondary reactions such as tar and char formation reactions (pyrolysis behaviour Type III). On the other hand, when the carrier gas has some oxygen content (CO_2 and/or steam), an increase in temperature can also promote a lower char yield (lower than the expected value) given the occurrence of gasification reactions as reported by several authors [67,157,172]. Even so, Williams et al. [52] reported that higher pyrolysis temperature under an inert atmosphere could volatilise some of the solid hydrocarbon content of the char, although there is no obvious mechanism for carbon loss with increasing temperature under pyrolysis conditions. The authors reported a decrease in the solid fraction yield and an increase both in the yield of gas and liquid as temperature was increased from 420 to 720 °C for each heating rate tested (5, 20, 40 and 80 °C/min). At 720 °C and 80 °C/min the solid yield was around 26.4 wt% and the fixed carbon and ash content of tyre were 30.30 and 2.40 wt% respectively. Similarly, Zabaniotou and Stavropoulos [154] observed a decrease in the solid yield with increasing temperature using a captive sample reactor at

atmospheric pressure (where it is possible to achieve nearly zero residence time at the final process temperature and rapid cooling of the gaseous products). The carrier gas used was He. They found an asymptotic value of 20 wt% while gas yield increased reaching an asymptotic value of 73 wt%, both at 830 °C. According to Cunliffe and Williams [54], the char evolution from tyre pyrolysis is linked to a number of factors, not only the temperature and the heating rate but also system specific parameters such as the size of reactor, the efficiency of heat transfer from the hot reactor surfaces to and within the tyre particles and the vapour residence time in the hot zone.

Besides the yield behaviour regarding temperature effect, the properties of the solid fraction also depend on many variables linked to the occurrence of secondary reactions. Also, tyre composition seems to influence the solid fraction since inorganic compounds can react as commented before for the temperature effect on the gas fraction. Likewise, as reported by Ucar et al. [69], depending on the tyre type (PCT and TT) the ash content varies being higher for the former type. Therefore, it is not surprising to find large different information in the literature about the properties of the pyrolytic CB. For instance, the last mentioned authors observed that the gross calorific value was higher for the TT (~34 MJ/kg) than for the PCT (~15 MJ/kg) when the pyrolysis was carried out at 550, 650 and 800 °C in a FBR. González et al. [56] observed a slightly decreased in the calorific value of the char (from 27.9 to 27.0 MJ/kg) with increasing temperature (from 550 to 700 °C) also using a FBR. Li et al. [58] reported a slightly decrease in the calorific value (from 30 and 31.5 MJ/kg) as the temperature increased from 450 to 650 °C using a RKR. The authors also revealed that temperature had little effect on the char size distribution. Around 83–84% of the char particles had fractions with sizes of less than 5.1 mm whilst the BET surface area was 89.1 m^2/g. They also showed that the volatile matter content decreased whilst the fixed carbon content increased with increasing temperature. Fernádez et al. [173] using a horizontal oven at 15 °C/min reported that the pyrolytic CB produced at 550 and 900 °C exhibited type IV isotherms characteristic of mesoporous materials (2–50 nm), without any remarkable influence of the pyrolysis temperature. BET surface area did not show any significant variation with the increase in temperature and it was around 68 m^2/g at 550 °C and 61 m^2/g at 900 °C. In contrast, López et al. [158] using a continuous CSBR observed a trend of increasing BET surface area with temperature. At 425 °C the BET surface area was 46.5 m^2/g whilst at 600 °C was 116.3 m^2/g. In the same way, Williams et al. [52] reported the same tendency that López et al. [158] but using a FBR. The surface area showed an increase as the pyrolysis temperature increased and this effect was more remarkable at higher heating rates.

3.2.1.4. Final remarks on the temperature effect. In conclusion, it has been reported that the reaction temperature in WT pyrolysis leads to different results in the yields as well as in the properties of the products depending on many other process variables. Three tendencies have been proposed in order to explain the behaviour of the pyrolysis process regarding the temperature effect on the products yields. The strict pyrolysis performance (pyrolysis behaviour Type I), without any extent of secondary reactions, shows an increase of the volatile products yield (condensable and non-condensable compounds) as the temperature increases (up to 500 aprox.) at expense of the solid fraction yield. Higher temperatures do not affect the pyrolysis products yield, although the gas fraction composition can be altered. Generally speaking, the yield to liquids, when the volatiles released are condensed, shows a maximum at around 450–500 °C. At higher temperature, the gas yield can increase as long as secondary reactions take place at expense of the liquid fraction (pyrolysis behaviour Type II). Simultaneously, the aromatic compounds in the liquid fraction increases.

3.3. Pressure

According to Buekens [31] a pressure increase on plastics feedstock pyrolysis leads to more viscous liquid products with a higher coking tendency as well as more secondary and dehydrogenation reactions. On the other hand, vacuum pyrolysis reduces the incidence of secondary reactions in the vapour phase in contrast to pyrolysis at atmospheric pressure. Under vacuum, the residence time of the volatiles pyrolysis products is shorter and so the secondary reactions are limited [58,62,74]. Consequently, the formation of undesired products such as carbonaceous deposits on the char surface are minimised and hence its surface area is improved as well as the amount of active sites is increased. In addition, the liquid yield with the vacuum process is also improved in comparison to the atmospheric pyrolysis process, whereas the yields of char and gas are lower [58,59,62,174].

López et al. [174] stated that the vacuum effect is explained by the fact that vacuum enhances diffusion toward the outside part of the volatiles formed within the porous structure of the tyre particle, which is due to the positive pressure gradient generated by vacuum for that flow. Thus, the faster diffusion of the volatiles inside the particle reduces their residence time and consequently, it must limit the occurrence of secondary reactions. According to Roy et al. [165], one major advantage of the vacuum pressure is the reduction of the pyrolysis temperature. In addition, vacuum pressure helps to reduce the mass flow rate of the inert gas improving the process viability. It is also lowering the requirements of the condensation device for collecting the liquid fraction as lower amount of energy is required to cool down the outlet stream [174].

Pure polyisoprene (NR) and a commercial rubber sample containing 52.2 wt% of polyisoprene, 31.0 wt% of CB and 5.4 wt% of SBR and others compounds were pyrolysed at 500 °C by Roy et al. [165] in a batch reactor at vacuum pressure. The total pressure was varied between 0.8 and 28.0 kPa. The yields of gas, liquid and solid changed little with the pressure, although at lower pressures less gas and more liquids were obtained. The pressure effect on tyre pyrolysis was mainly reflected in both the liquid composition and the characteristics of the pyrolytic CB. Lower pyrolysis pressure increased the amount of D,L-limonene. Similarly, the surface chemistry of the solid fraction was composed mainly of CB became similar to that of the commercial CB normally used in tyre manufacture. Likewise, Zhang et al. [62] using a FBR also showed that under vacuum conditions (3.5–4.0 kPa) the pyrolytic CB had a surface area comparable to commercial CB, although its ash concentration was much higher. In addition, the concentration of D,L-limonene in the liquid fraction increased as pyrolysis pressure decreased. The authors also observed that a certain amount of carbonaceous materials was formed in the solid fraction and attributed this behaviour to the occurrence of secondary repolymerisation reactions. Thus, even at vacuum pressure, secondary reactions can appear giving way to either carbonaceous deposits formation or to a higher gas yield.

As a final conclusion, it is worth noting that lower operating pressures can reduce the occurrence of secondary reactions, but not totally avoided. Generally speaking, the lower the pressure, the lower the role of secondary reactions. Also, a decrease in the process pressure may lead to a reduction in the process temperature, decreasing the thermal energy demand of the pyrolysis process.

3.4. Particle size

Although it is well-known that particle size interacts with the pyrolysis kinetics and the heat internal transfer (affecting the

pyrolysis products yields and characteristics), there are few studies regarding the influence of particle size on the performance of the tyre pyrolysis process. According to Oyedun et al. [175] this can be justified by the fact that a wide literature on tyre pyrolysis has been conducted under heat transfer rates that consider fast pyrolysis conditions and for this reason the particle size has not been widely studied.

It is generally assumed that in thermochemical processes, small particles present an isothermal behaviour and have no limitation to internal mass transfer (no mass or temperature gradients inside the material), whilst the opposite may be found in large particles [64]. According to Beaumont and Schwob [176], the temperature gradient involved when the pyrolysis process is carried out with larger particles sizes could be justified by the effort of particle size on heat transfer: the coarser the particles, the slower the heating, and thus, the pyrolysis reaction is accomplished at a lower temperature. The heat transfer rate requirements impose particle size limitations [51] and hence, heat can flow only to a certain depth in coarser particles at the available pyrolysis time in comparison with almost complete degradation of the small ones [177]. In consequence, the rubber core of the larger pieces remains unchanged affecting the char reactivity and the pyrolysis conversion grade. Under this situation lower yields of both liquid and gas are achieved. Therefore, and as pointed out by Bouvier et al. [107], the size of tyre particles and pyrolysis conversion are inversely related. For instance, Dai et al. [55] using a CFBR at 500 °C found a higher tyre conversion grade and a decrease in the pyrolytic CB yield (from 45 to 30 wt%) when the tyre particle size was reduced from 0.8 mm to 0.32 mm. Likewise, gas and liquid fractions were lower for 0.8 mm. According to the authors, smaller particle size provided more reaction surface for char reduction, which also led to more gas product. Similarly, Barbooti et al. [177] reported more liquid yield for lower particle sizes using a FBR at 0.35 m^3/h of N_2 in the temperature range between 400 and 460 °C.

Moreover, cylindrical tyre particles with diameters between 7.5 and 22 mm were devolatilised in a macro-TG reactor at temperatures between 490 and 840 °C in an inert atmosphere by Larsen et al. [64]. The effect of particle size and surrounding temperature on the rate of devolatilisation was observed to be significant. Larger particle diameters and lower temperatures increased the pyrolysis time. Oyedun et al. [175] also showed a remarkable effect of the particle size on the pyrolysis time. They coupled a particle heat transfer model with a kinetic model in order to optimise the particle size for different pyrolysis times and heating rates. At 500 °C and 5 °C/min the pyrolysis time was around 1.5 and 2.5 h for particles with a radius of 10 and 50 mm respectively. Heating rate also showed a notable influence. At the same temperature and 10 °C/min the pyrolysis time was around 0.8 and 1.9 h for the above mentioned particle radius. Thus, particle size effect on tyre pyrolysis depends on both the heating rate and temperature. It seems that as the heating rate increases, the process can be conducted with higher particle sizes.

Additionally, secondary reactions can also take place depending on the pyrolysis conditions applied. In this way, Islam et al. [51] using a FBR at 475 °C found lower a liquid yield for particles of 2 cm^3 than for particles of 4 cm^3. Also, both the pyrolytic CB and the gas fraction were higher for 2 cm^3 than for 4 cm^3. The authors attributed this behaviour to the quick devolatilisation rate of the lower particles given its higher reaction surface and consequently the possible occurrence of any secondary reaction as thermal cracking. In conclusion, the particle size effect is related to pyrolysis reaction time, volatiles residence time, heating rate and temperature. In many pyrolysis studies a low particle size is preferred in order to minimise the mass and energy phenomena effects and thus, to achieve a higher conversion grade and primary pyrolysis products. However, depending on the heating rate and the volatiles residence time, lower particle sizes can lead to a quick devolatilisation rate and consequently to possible secondary reactions.

3.5. Heating rate

Heating rate is a key variable on the pyrolysis reaction since notably affects the reaction rate and determines the temperature profile within the particles. Generally speaking, increasing the heating rate results in a shift to higher temperatures of the weight loss profile in a TG analysis (Fig. 4) [9,15,52,61,92]. This means that the degradation rate increases as the heating rate is increased and also that the temperature at which maximum devolatilisation begins and ends is affected by the heating rate. According to Williams and Besler [15], this phenomenon is attributed to the combined effects of the heat transfer and the changes in the kinetics of the decomposition, resulting in delayed decomposition. Thus, higher heating rates in fast pyrolysis, besides to promote an increase in the amount of volatiles cumulatively released [61], lead to an increase in the process temperature in comparison with slow pyrolysis. However, as previously discussed, this could encourage secondary reactions and as possible consequence, a higher gas fraction. For this reason, the residence time of the volatiles released in fast pyrolysis must be lowered in order to minimise secondary reactions and maximise the liquid fraction derived from the condensable gases. Accordingly, Williams et al. [52] and Senneca et al. [61] concluded that the characteristics of the vapours released in the pyrolysis process were mainly influenced by the heating rate as well as by the balance between primary and secondary devolatilisation products.

In addition, the heating rate is directly related with the characteristics of the reactor and the process. In continuous reactors as AR, fluidised beds reactors (BFBR and CFBR), CSBR, RKR (with homogeneous temperature levels) and in the ablative process, where the temperature is fixed at some value and is kept constant along the process, the heating rate is not a direct process parameter of control. In this type of reactors the heating rates are very high and mainly depend on the reactor characteristics. For instance, the continuous ablative reactor heats solid particles to a high temperature by ablation on a hot surface in less than 1 s [178]. Even so, heating rate is one of the most studied parameters in pyrolysis because besides to affect the products yields (as shown before in types of pyrolysis) also influences the pyrolysis completion time and the energy required to drive the process. In this way, Cheung et al. [93] by means of a kinetic and heat transfer model reported that lower heating rates required less energy to complete the pyrolysis, although the pyrolysis time increased. In contrast, higher heating rates needed more energy whilst the pyrolysis time decreased.

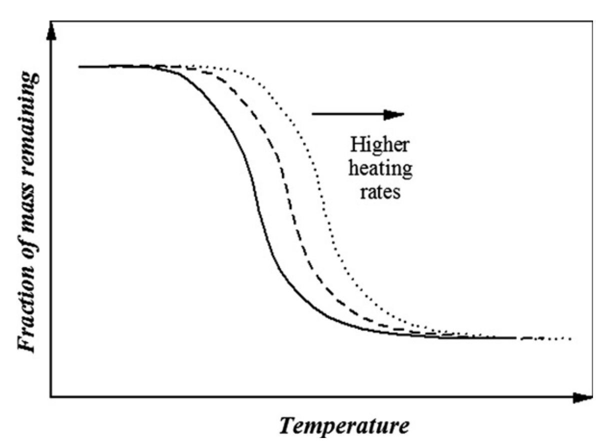


Fig. 4. Heating rate effect on the pyrolysis in a TG analysis.

A general behaviour is usually adopted to explain the heating rate effect on pyrolysis. Low heating rates may conduct to some resistance to mass or heat transfer inside the particle. Heat and mass transfer restrictions are minimised at higher heating rates, increasing the liquid fraction yield and decreasing solid fraction yield as occur in fast pyrolysis. Senneca et al. [61] showed that increasing the heating rate and feedstock particle size, lead to a more uniformity pyrolysis process without temperature and internal pressure gradients. The authors studied the effect of different heating rates (5, 20, 100 and 900 °C/min) and particle sizes (1 and 3 mm) using TG analysis. At 600 °C the pyrolytic CB yield for particles of 1 mm was approximately 37 wt% regardless the heating rate. For the 3 mm size samples the char yield was slightly more scattered, although it kept around the same value of 37 wt% when pyrolysis was carried out at heating rates higher than 20 °C/min. However, this value increased up to 40 wt% at 5 °C/min. The authors ascribed this behaviour to cyclisation/crosslinking reactions that favoured the growth of the pyrolytic CB.

It is worth noting that the internal particle heating occurs from the outer surface (where pyrolysis decomposition reaction takes place) to core. Thus, as the pyrolysis time progresses the reaction progress up to the core. The generated vapours released during pyrolysis can diffuse through pore and out of the particle to the bulk of gas. Simultaneously, homogeneous and heterogeneous secondary reactions can occur inside the porous particle and in the bulk of the gaseous phase. Therefore, there is a high sensitivity in the appearance of secondary reactions by varying heating rate and for this reason the literature survey shows a wide distinction. For instance, Williams et al. [52] assessed the heating rate effect (5, 20, 40 and 80 °C/min) with different pyrolysis temperatures (300, 420, 600 and 720 °C) in a FBR. The calorific value of the gas fraction obtained at 720 °C was between 36.5 and 64.7 MJ/m^3 at heating rates of 5 and 80 °C/min respectively. Likewise, the liquid fraction showed more aliphatic and less aromatic compounds as the heating rate increased (for runs conducted at 5, 20 and 40 °C/min) and this behaviour suggests that the pyrolysis reaction was conducted without any secondary reaction influence. Similarly, Murillo et al. [63] did not find a remarkable influence of the heating rate on the total tyre conversion and both the yield and properties of the liquid fraction. The aromatic compounds of the pyrolytic liquid fraction prevailed around 70 wt%. They used a FBR operated at 500 °C, 15 min of pyrolysis time, 0.56 m/s of superficial velocity of N_2 and different heating rates (25, 100 and 300 °C/min). However, González et al. [56] using a FBR observed that increasing the heating rate from 5 to 20 °C/min gave similar results to those obtained when temperature increases, since the gas fraction increased as the heating rate increased (pyrolysis behaviour type II). It was also reported an increase in the H_2, CO, CH_4, CO_2, C_2H_4 and C_2H_6 concentration.

Once again, as commented for the temperature and the particle size effect, the heating rate effect on tyre pyrolysis can show different behaviours and all of them are mainly associated with the occurrence of secondary reactions promoted by the interaction of other variables, mainly the volatiles residence time.

3.6. Carrier gas flow rate and type

The presence of an inert gas in the pyrolysis process allows controlling the occurrence of secondary reactions such as thermal cracking, repolymerisation, recondensation and char formation (this last one, for example, by the Boudouard reaction) [52,56] and also, guaranteeing the absence of oxygen that could lead to some kind of oxidation. The flow rate has a direct effect in both the superficial velocity and the residence time of the evolved products released during the pyrolysis process. Generally speaking, as the flow rate increases, the superficial gas velocity increases and consequently the vapour residence time decreases. Thus, higher flow rates remove these vapours quicker from the reaction zone and hence minimise secondary reactions. In a large-scale FBR, Cunliffe and Williams [54] pointed out higher liquid yields (56.9 wt% at 525 °C and 5 °C/min of heating rate) as the carrier gas was increased. The authors stated that the volatiles released after tyre pyrolysis were removed by the N_2 flow rate before significant secondary char forming reactions could occur. In the same way, Islam et al. [51] found that when the carrier flow was decreased in a FBR and consequently the volatiles residence time raised, the liquid and char yields decreased whilst the gas yield increased indicating the occurrence of secondary reactions.

Regarding the type of carrier gas, if a non-inert gas is used such either steam or pyrogas, the characteristics of the products are also affected since some homogeneous or heterogeneous reactions can take place. Kaminsky et al. [170] using a BFBR found that the use of steam gave higher values for C_2H_4 and C_3H_6 than the use of pyrogas, although the H_2S concentration showed a reduction when pyrolysis gas was used. Ogasawara et al. [157] fed steam (0.75 mg of water/s per gram of sample) and He (0.67 cm^3/s) at 900 °C in a FBR. They found a char yield (9 wt%) lower than the produced in conventional tyre pyrolysis under non-oxidative conditions but with a very high surface area of 1260 m^2/g. H_2 and CO were the major components of the gas fraction and aliphatic hydrocarbons and alkylbenzenes were the prime components of the liquid one. Similarly, Betancur et al. [67] using CO_2 as carrier gas, found that for temperatures higher than 760 °C the CO_2 started to oxidize the remaining solid fraction. It was obtained an activated carbon with a 414 m^2/g surface area at 900 °C, 150 mL/min of CO_2 and 180 min of pyrolysis time. In addition, it was demonstrated that there is none influence of CO_2 over the devolatilisation of tyres at temperatures lower than 760 °C. In the same way, Lucchesi and Maschio [104] reported a high desulphurisation effect on the char and liquid fractions using CO_2 as carrier gas. The sulphur content on the solid fraction was around 1.8 and 0.3 wt% under N_2 and CO_2 atmospheres respectively. For the liquid fraction, the sulphur content was 0.6 and 0.2 wt% respectively. The CO_2 atmosphere shifted the sulphur to the gas fraction. Mastral et al. [11] reported that there are no remarkable differences using H_2 or N_2 over the total conversion of tyre independently of the reactor type (swept FBR and tubing bomb reactor and also in a magnetically stirred autoclave installation). However, H_2 pressure showed an important effect in the liquid composition becoming lighter: more saturates and less aromatics and polar compounds. Also, higher liquid yields were obtained. The increase in liquid yield at high H_2 pressures was attributed to the tyre-derived radicals being stabilised preventing retrogressive/recombination reactions that could lead to some heavier liquids and lighter hydrocarbon gas formation.

As a conclusion, the carrier gas seems to be an important variable to control the appearance of secondary reactions. Generally speaking, it is expected that higher flow rates prevent secondary reactions since the volatiles residence time is decreased. On the other hand, as it is expected, a non-inert carrier gas can lead to some homogeneous and heterogeneous secondary reactions such as char gasification or thermal cracking. Besides the proper nature of the carrier gas, some physical quantities such as pressure and temperature can also exert an important role on the distributions and properties of the pyrolysis products as showed for the H_2 and CO_2 respectively.

3.7. Residence time of the volatiles inside the reactor

As mentioned above, the residence time of the volatiles (also named vapours) is directly linked with the carrier gas flow rate

and the type of reactor due to their unique intrinsic characteristics. The residence time of the volatiles inside the reactor is controlled by the flow rate of the carrier gas and presents an inversely proportional relationship. As shown before, higher residences time can favour some secondary reactions altering the products distributions and properties. For instance, Aylón et al. [179] compared the tyre pyrolysis performance using an AR and a FBR. A more severe cracking of the primary pyrolysis products occurred in the AR mainly due to the longer volatiles residence time. This fact was evidenced due to the decrease of the liquid fraction yield (from 54.6 to 43.2 wt%) and the increase of the gas yield (from 7.5 to 17.1 wt%) when the pyrolysis was performed in AR instead of in the FBR, both at 600 °C. Likewise, Dai et al. [55] evaluated the effect of different residence times (1, 3 and 5 s) using a CFBR and varying the feed position and the gas velocity. The main trend observed was that H_2, CO and light hydrocarbon gases increased with the increase of the residence time, whilst CO_2 decreased slightly. The authors attributed this behaviour to the secondary reactions including char reduction, tar cracking and shift reaction, among others. Similarly, Conesa et al. [155] using He as carrier gas in a BFBR showed an increase in the production of H_2, CH_4 and others gaseous compounds, when the residence time of the volatiles increased. However, the total gas yield was lower at 900 °C than that at 800 °C regardless the residence time. This behaviour was attributed to the cracking of tars to char since the solid fraction increased when temperature increased. In the same way, Islam et al. [51] studied the influence of the volatiles residence time (5, 10, and 20 s) by means of a sweeping gas flow (8. 4 and 2 L/min). They found that the liquid and char yields decreased while the gas yield increased when the vapour residence time increased from 5 to 20 s. This behaviour was similar to those reported when the carrier gas flow rate decreased. The authors also highlighted that a longer contact time between the volatiles and the chars could favour the Boudouard reaction, leading to a reduction in the char yield.

3.8. Pyrolysis time

According to Aylón et al. [8] the pyrolysis time, also referred as residence time of the tyre inside the reactor or simply reaction or dwell time, is a key factor in order to scale up an industrial system. Lower residence time involves lower reactor volumes and therefore a lower cost of the system. Likewise, pyrolysis time is associated to the particle size as shown before. Generally speaking, it is expected that bigger particles need longer reaction times than lower ones to reach the same pyrolysis conversion grade.

Similarly, as mentioned above, there is also an important role of the heating rate which is linked with the type of reactor. Aylón et al. [179] compared the results obtained in FBR and AR using an average particle size of 2 mm. The authors observed that total rubber conversion was achieved in both systems although the pyrolysis time in the FBR (30 min) was longer than in the AR (3.7 min). In ARs, the variation of the pyrolysis time involves the variation of the volatiles residence time. This variation is due to the increment of the free volume inside the reactor when the pyrolysis time decreased [8], which consequently gives a higher volatiles residence time. For this reason, in this type of reactors, the pyrolysis reaction time and the volatiles residence time are linked. Therefore, the pyrolysis time is also related with the intrinsic characteristics of the pyrolysis reactor. As stated by Olazar et al. [180] the equipment typically used for kinetic studies (TG balance) operates under conditions that are different to those of a pilot or industrial plant, where particle heating is almost instantaneous and the gas–particle contact is much more turbulent. In view of this, they reported the evolution of different pyrolysis products (aromatics (C_{10-}), pyrolytic CB, gas (C_{4-}), intermediate compounds, non-aromatic liquid (C_5–C_{10}) and tar (C_{10+})) with the pyrolysis time at different pyrolysis temperatures (425, 500, 550 and 610 °C) using a pilot plant (CSBR). They, besides having proposed a satisfactory model for the tyre pyrolysis products evolution (useful for the industrial design of the spouted bed technology), showed that when temperature increases the pyrolysis time decreases since the internal particle heating is higher. Similar results were reported by Cheung et al. [93] regarding the decrease of the pyrolysis time as temperature increases. Even though, it is worth to point out that both longer pyrolysis time and higher temperature negatively affect to the quantity of heat required to complete the pyrolysis and consequently to the process efficiency.

Therefore, it can be concluded that longer reaction times should be used for processing larger size tyre particles although an increase in the temperature or heating rate could lead to a shorter reaction time. However, as it has been mentioned along this work, these variables can exert a notably influence in the appearance of secondary reactions. Besides that, each pyrolysis reactor has an unique intrinsic characteristics and for this reason the pyrolysis time variation can alter key parameters such as the volatiles residence time. The strict effect of the pyrolysis time depends on the particle size and also on the reactor technology.

4. Characteristics of the tyre pyrolysis products

4.1. Tyre liquid from pyrolysis

The liquid fraction is considered the most abundant fraction obtained from the WT pyrolysis process. According to Mirmiram et al. [13] the liquid from tyre pyrolysis consisted of (i) the processing liquid as part of the tyre formulation, (ii) organic additives, and (iii) tyre pyrolysis products. This liquid is dark brown-coloured product, which resembles petroleum fractions [50]. As shown in Table 10, liquid from tyre pyrolysis can reach 44 MJ/kg of energy content depending on the tyre composition and the process conditions. Thus, the pyrolysis liquid has a higher calorific value than the WT from which is recovered. Also, it could show similar properties to those of a light fuel liquid with similar calorific value and sulphur content [50,54], which would encourage its use as replacement for conventional liquid fuels. In fact, studies carried out by Williams et al. [118] showed good results regarding its combustion in a long ceramic-lines furnace for several working hours without problems (1.6 m in length and 0.5 m internal diameter), although NOx and SO_2 emissions (374 and 530 ppm respectively at 2.1% O_2) were higher than using a diesel fuel (131 and 110 respectively at 2.1% O_2). The nitrogen and sulphur contents in the tyre liquid corresponded to 1.45 and 0.45 wt% respectively, whilst diesel fuel were 0.05 and 0.2 wt% respectively.

Sulphur compounds formation in the pyrolytic liquids is due to the thermal degradation of additives such as vulcanisation agents and accelerators added during the tyre manufacturing process [78]. Similarly, higher concentrations of inorganic compounds such as fluorine and chlorine are usually present in the tyre liquid as shown in Table 10. Benallal et al. [114] observed that sulphur compounds in the tyre liquid obtained under vacuum conditions were concentrated in the light portion of the naphtha fraction (boiling point around 160 °C) in contrast with petroleum, where the sulphur compounds are concentrated in the heavy ends with boiling point higher than 160 °C. The most prominent sulphur compounds identified by the authors in the pyrolytic naphtha fraction were 2-methylthiophene, 3-methylthiophene, 2-ethylthiophene, 2.5-dimethylthiophene, 2.4-dimethylthiophene, 2.3-dimethylthiophene, 3-ethylthiophene, 2-isopropylthiophene, 2-*tert*-butylthiophene and benzothiazole. According to Pakdel et al. [78] approximately 60–80%

Table 10
Elemental and calorific value of the liquid fraction reported in literature.

Liquid yield (wt%)	Elemental analysis on as received basis (wt%)						Inorganics (ppm)			CV (MJ/kg)	Pyrolysis temperature (°C)	Reactor type	Ref.
	C	H	N	S	O	H/C	Cl	F	A				
38.00[c]	85.60	10.10	0.40	1.40	2.10[e]	1.42	n.r.	n.r.	n.r.	42.10[a]	500	FBR	[50]
53.10	87.90	10.10	0.50	1.30	0.1		100	100	0.002	41.20[a]	600	FBR	[54]
44.60	84.55	9.59	0.64	1.26	3.96[e]	1.36	n.r.	n.r.	t	41.00[b]	550	RKR	[58]
46.10[f]	85.40	11.40	0.40	0.60	n.r.	1.60	n.r.	n.r.	n.r.	43.27[a]	550	FBR[a]	[66]
38.00	84.90	9.60	0.40	1.60	3.50	1.36	n.r.	< 100	n.r.	40.77[a]	550	FBR	[68]
48.40[c]	87.57	10.35	< 1	1.35	n.r.	1.42	n.r.	n.r.	n.r.	41.60[a]	650	FBR	[69]
56.00[d]	86.47	11.73	< 1	0.83	n.r.	1.63	n.r.	n.r.	n.r.	42.40[a]			
45.00[c]	86.50	10.80	0.50	0.80	2.20	1.50	130	n.r.	t	43.70[a]	520	Pyrocycling™	[149]
43.00[d]	87.90	11.20	0.70	1.00	0.20	1.53	100	n.r.	0.005	44.80[a]	485	process	
43.20	85.27	10.35	1.01	0.99	n.r.	1.46	n.r.	n.r.	n.r.	n.r.	600	AR	[179]
54.60	83.45	10.31	1.05	0.99	n.r.	1.48	n.r.	n.r.	n.r.	n.r.		FBR	

n.r., not reported; A, ash in wt%; t, traces.

[a] Higher.
[b] Lower.
[c] Passenger car tyre.
[d] Truck tyre.
[e] Oxygen plus others.
[f] Mixture between passenger car and truck tyres.

of these sulphur-containing compounds in the tyre liquid could be removed during a primary distillation. Williams et al. [52] reported a sulphur concentration around 1.1 wt% in the tyre liquid obtained in a FBR which represented a 60% of the sulphur content in the WT. Kawakami et al. [47] using a RKR collected light and heavy liquid fractions with sulphur contents of 1.01 and 1.65 wt% respectively. Taking into account a liquid yield of 53 wt%, sulphur distribution in tyre liquid were around 25 and 30 wt% respectively. Similarly, Kaminsky and Sinn [102] reported a sulphur content lower than 0.4 wt% in the aromatic fraction of the liquid obtained in a indirectly heated BFBR at 720 °C using whole tyres. Cunliffe and Williams [54] pointed out sulphur contents of 1.4 wt% for a pyrolysis temperature from 450 to 475 °C. A decrease to 1.3 wt% was found for temperatures from 500 to 600 °C. More results regarding sulphur concentration in tyre liquid are showed in Table 10.

Tyre liquid generally presents a very small amount of oxygen content and a high H/C atomic ratio (around 1.5) representative of aliphatic and aromatic compounds (Table 10). As it has been discussed before, the relative proportion of aromatics increases when pyrolysis temperature increases, whilst the aliphatic fractions decrease for pyrolysis behaviours type II and III, where there is an occurrence of secondary reactions. According to Rodriguez et al. [50] the increase of these aromatic compounds in the tyre liquid is attributed to the recombination reactions that take place among aliphatic and aromatic free radicals and also to the cyclisation of aliphatic chains. This was also pointed out by Mastral et al. [12] who suggested that the composition of the aromatic fraction could be affected by cyclisation and aromatisation reactions of the primary volatiles. Similarly, some works [66,69,174] highlighted that the aromatic content in tyre liquids is given by the aromatic nature of the rubber (although just one aromatic ring is present in the SBR monomer [12,63]) and also by the cyclisation of olefins structures followed by dehydrogenation and Diels–Alder reactions. Unapumnuk et al. [24] associated the mechanisms for aromatic hydrocarbons formation with polymer degradation, methyl displacement and also with the Diels–Alder reactions. In this way, several authors [52,54,78,97,117,158,181] have suggested the Diels–Alder type reaction mechanism as the cause for the increase in aromatic content as the pyrolysis temperature increases.

Generally speaking, tyre liquid is a mixture of organic compounds of C_5–C_{20} or even more carbons with different proportions of aromatic and aliphatic compounds [50,56,63] depending, besides the process conditions, on tyre composition since the proportion between these two compounds can show different trends as discussed before (SBR degradation gives way to a higher amount of aromatic hydrocarbons). Likewise, Kyari et al. [16] also reported significant concentrations of alkylated benzenes, alkylated naphthalenes, alkanes and alkenes. Similarly, Rodriguez et al. [50] observed nitrogenated and sulphur-containing compounds that Laresgoiti et al. [182] associated with the accelerators used in tyre manufacture. López et al. [174] defined the tyre liquid as a complex mixture of hydrocarbons whose individual composition is generally low, but it also contains interesting hydrocarbons in a high proportion such as isoprene, limonene and styrene, as also stated by Conesa et al. [60].

Tyre liquid can be added to petroleum refinery feedstock or to be used as a source of refined chemicals such as BTX and limonene [4,15,56]. It is an established fact that these chemicals are used as primary feedstock to produce plastics, resins, surfactants and pharmaceuticals compounds among others. Similarly, it may be processed in a refinery hydrocracking units for reducing aromatic and olefin content [158]. The application of tyre derived liquid in coke production can also be found. Chaala and Roy [116] showed the technical feasibility of the pyrolysis liquid (the heavy fraction of the liquid obtained in vacuum pyrolysis, boiling point > 350 °C) as a raw material for a good quality coke production regarding low sulphur, ash and metal contents including vanadium that is the main contaminant of commercial petroleum cokes. In addition, the coking of this liquid gave other valuable products such as a new liquid fraction and a high calorific value combustible gas. According to the authors, the new liquid fraction can be divided into a highly aromatic naphtha portion (initial boiling point 205 °C), a middle distillate (boiling point 205–350 °C) and a heavy gasoil fraction (boiling point > 350 °C) that showed a high asphaltene content.

4.1.1. Limonene role

Limonene ($C_{10}H_{16}$) is a value-added product present in the tyre pyrolysis liquid that is commonly used in the formulation of industrial solvents, resins, adhesives, cosmetics and as a dispersing agent for pigments. Limonene is a cyclic terpene that contains two units of isoprene [173]. It is also used as feedstock for the production of fragrances and flavourings [4,54,112].

Limonene exists in the form of D,L-limonene (dipentene) and D- and L-limonene, the dipentene racemic form and both have the same physical properties [54,78,112].

It is usually accepted that D,L-limonene is one of the major products in the tyre liquid [54,78] and its formation depends on the pyrolysis pressure, temperature and vapour residence time inside the reactor, as well as the sample size and composition. D,L-Limonene yield decreases with increasing temperature due to the occurrence of secondary reactions. Thus, D,L-limonene is transformed into aromatic compounds such as trimethylbenzene, *m*-cymene and indane, among others [78]. However, at lower pyrolysis pressure and short volatiles residence time, the occurrence of secondary reactions are minimised and consequently D,L-limonene yield is increased. For this reason, limonene concentration is higher under vacuum pyrolysis than under atmospheric pressure [78,112,114,165]. Zhang et al. [62] also observed that the content of limonene is very sensitive to pyrolysis temperature and pressure. At a pressure of 3.5–4.0 kPa, the content of limonene in the liquid fraction decreased from 11.97 to 4.72 wt% when pyrolysis temperature increased from 450 to 550 °C. At a pyrolysis temperature of 500 °C the content of limonene decreased from 11.73 to 7.8 wt% when the pyrolysis pressure increased from 3.5 to 10 kPa. Cunliffe and Williams [54] found that limonene was the major component of the tyre liquid obtained in a large-scale FBR, representing 3.1 wt% at 450 °C and decreasing to 2.5 wt% of the total liquid at 600 °C. Arabiourrutia et al. [183] reported a decrease in the liquid fraction as temperature increased in a CSBR operated a different temperatures (425, 500, 550 and 610 °C) in batch operation. The C_{10} lump in this fraction, related with D-limonene, decreased with temperature from 28.00 wt% at 425 °C to 17.99 wt% at 610 °C. At these conditions, the D-limonene yield was 23.39 and 5.66 wt% respectively. Similarly, Li et al. [58] using a RKR observed a limonene concentration in the pyrolysis liquid of 5.4 wt% at 450 °C. At 650 °C it decreased up to 0.07 wt%.

In the same way, Roy et al. [165] reported 16.6 wt% of limonene in the liquid fraction when pure polyisoprene was pyrolysed under vacuum in a batch reactor. For a commercial rubber sample containing 52.2 wt% of polyisoprene, 31.0 wt% of CB, 5.4 wt% of SBR and other compounds, the limonene concentration decreased up to 5.0 wt% for the same operational conditions (500 °C and 0.8 kPa). Many different reaction pathways for limonene production from tyre pyrolysis have been reported in literature [12,62,77–79] and many of them agree that the polyisoprene (NR) content in the tyre is the main source of limonene in the liquid tyre pyrolysis [12,62,79,112]. Kwon and Castaldi [79] besides relating the limonene with the polyisoprene rubber, associated the styrene content with the SBR. They found that chemical species such as limonene and 1-methyl-4-(1-methylethyl)-benzene were only observed during polyisoprene pyrolysis whilst styrene and 4-ethenylcyclohexene were observed during SBR pyrolysis.

4.1.2. PAHs presence

Taking into account the amount of aromatic compounds in the tyre liquid, the presence of polycyclic aromatic hydrocarbons (PAHs) is not surprising. For instance, Williams et al. [52] reported the presence of alkanes, alkenes and aromatic compounds such as benzene, toluene, xylene, styrene and 2–6 ring PAH together with alkyl derivatives in the liquid derived from the pyrolysis of tyres. Kaminsky and Sinn [102] pointed out concentrations of naphthalene (0.85 wt%), fluorene (0.16 wt%), phenanthrene (0.29 wt%) and pyrene (0.21 wt%) in the liquid derived from tyre pyrolysis carried out at 750 °C in a BFBR. Laresgoiti et al. [182] also showed the presence of naphthalene, fluorene, phenanthrene and diphenyls when the process was carried out in a FBR. Similar results were reported by Li et al. [58] using a continuous RKR.

PAHs dependency with temperature has been also investigated. In this way, Cypress and Bettens [97] carried out waste rubber pyrolysis between 400 and 450 °C followed by a post-cracking (from 600 to 800 °C) of the volatiles released in the previous stage. They found that concentrations of PAHs (naphthalene and phenanthrene) increased with increasing post-cracking temperature. Likewise, Cunliffe and Williams [54] using a large-scale FBR reported that the total PAHs content of the liquids increased from 1.53 to 3.43 wt% of the total liquid as the pyrolysis temperature was increased from 450 to 600 °C. Naphthalene, fluorene and phenanthrene concentrations increased from 465 to 1630 ppm, from 280 to 605 ppm and from 95 to 315 ppm respectively. Biologically active compounds such as methylfluorenes, tri- and tetra-methylphenanthrenes and chrysene were also identified in significant concentrations. Similarly, Williams and Taylor [117] performed WT pyrolysis experiments in two steps aiming the secondary reactions comprehension from the PAHs formation point of view. The evolved pyrolysis vapours were passed directly to a second FBR where different temperatures were evaluated (from 500 to 720 °C). According to the authors, as the secondary reactor temperature was increased, the total concentration of PAHs also increased from 1.4 to 10.1 wt%. and its formation was attributed to the Diels–Alder type reaction involving the aromatisation of olefinic compounds. The most marked increase in concentration occurred between 640 and 700 °C. The authors also highlighted a considerable effect of the volatiles residence time in the PAHs formation. As for the aromatisation pathway, the Diels–Alder type reaction mechanism involving cyclisation of alkenes and dehydrogenation was suggested by many authors to explain the PAHs formation [54,78,97,117,184].

According to the literature surveyed, aliphatic compounds are aromatised to PAHs as temperature increases and its formation seems to be unavoidable. However, Aylón [185] did not find the presence of PAHs in the liquid derived from WT using an AR, and this fact was attributed to the short volatiles residence time reached in this type of reactor. In the same way, Arabiourrutia et al. [183] highlighted the low yield of PAHs obtained at 500 °C in a CSBR and this behaviour was ascribed to the short residence time of the volatiles and the efficient performance of this type of reactor regarding heat and mass transfer. Therefore, some disagreements are found in literature and this could be attributed to the intrinsic characteristics of the reactor type and the analytical technique used as reported by Callén et al. [186]. Tyre composition also exerts a notably influence in the PAHs formation as reported by Kwon and Castaldi [166]. According to the authors, the molecular structure of SBR consists of a butadiene backbone supporting an aromatic ligand, which serves to accelerate PAHs formation, and for this reason it is expected a major PAHs concentration in tyre pyrolysis with higher SBR contents. They also stated that cyclisation by a Diels–Alder reaction is not the dominant reaction during decomposition of SBR.

4.1.3. Liquid fractionation

Liquids derived from tyre pyrolysis are a mixture of aliphatic, aromatic and polar compounds with a boiling point ranging between approximately 70 and 400 °C. For this reason, it is difficult to find possible applications different from their direct combustion without a purification or separation step previous to their commercialisation [152]. Generally speaking, a typical distillation curve shows a mixture of gasoline and diesel fuels with a wide range of boiling points that consequently reflects the fact that the tyre liquid is an unrefined hydrocarbon (Table 11).

Table 11
Pyrolysis liquids distillation behaviour reported in literature.

Average fraction cuts			Pyrolysis temperature (°C)	Type of reactor	Distillation system	Observations	Ref.
Ligh (< 200 °C)	Medium (200–350 °C)	Heavy (> 350 °C)					
58[a]	26[a]	6[a]	500[d]	FBR	ASTM D3710 standard test (simulated distillation method)	Distillation temperature between 105 and 375 °C (aprox.). Tyre liquids are unrefined and consequently have a wide range of boiling points	[16]
30[a]	30[a]	34[a]	500[b]	FBR	Automatic distillation test at atmospheric pressure	Distillation temperature between 78 and 388.7 °C. Tyre liquid was not comparable as diesel oil given the higher proportion of low boiling products	[50]
50[a]	45[a]	5[a]	475[c]	FBR	TG analyzer and ASTM D2887-89 standard test method	The pyrolytic liquids can be blended with the gasoline or diesel fuels after treatment such as desulphurization and hydrogenation or blending them with petroleum refinery streams	[51]
39[e] 42[e]	32[e] 33[e]	28[e] 24[e]	500 600	RKR	True-boiling-point autoclave device	The tyre liquid was much lighter than the crude oil since it only contains around 25 wt% of heavy fraction	[58]
60[a] 60[a]	35[a] 35[a]	5[a] 5[a]	550[b] 550[f]	FBR	Simulated distillation	Initial boiling point for both (PCT and TT) were lower than diesel fuel. Liquids from PCT and TT contained about 50 and 40 vol% of gasoline (boiling point range < 172 °C)	[69]
45[a]	35[a]	–	600	AR	ASTM D2887-04 standard test (simulated distillation method)	Distillation temperature up to 340 °C (aprox.)	[179]
30[a]	55[a]	15[a]	500	FBR	n.r.	Distillation temperature higher than 400 °C. Tyre liquid showed a final distillation temperature higher than diesel and for this reason it is expected a slower combustion behaviour	[187]

n.r., not reported.
[a] vol%.
[b] Passenger car tyre.
[c] Motorcycle tyre.
[d] Mixture of different tyre brands.
[e] wt%.
[f] Truck tyre.

Tyre pyrolytic liquid can be fractionated in order to indentify both the similitude with conventional fuels as gasoline and diesel and possible applications different from its direct combustion. Several results and conclusions can be found in the literature regarding the distillation behaviour as shown in Table 11. Differences among the several works are also ascribed to the pyrolysis conditions and tyre composition as well as the methodology used since many results were obtained from simulated distillation and real distillation tests. For instance, Laresgoiti et al. [182] performed an atmospheric pressure distillation test for the liquids obtained in a 3.5 dm^3 autoclave at 500 °C. They found that around 20 wt% of the tyre liquid could be classified as light naphtha (< 160 °C) whilst around 10 wt% as heavy naphtha (160–204 °C). Benallal et al. [114] reported that distillation of the pyrolytic liquids obtained at 510 °C and a total pressure of 2–20 kPa, yielded ~20 wt% of light naphtha (boiling point 160 °C), 6.8 wt% of heavy naphtha (160–204 °C), 30.7 wt% of middle distillate (204–350 °C) and 42.5 wt% of bottom residue (> 350 °C). Murillo et al. [152] showed a process for the separation of valuable gas and liquid fractions from the volatiles released in tyre pyrolysis by using commercial process simulation software (Hysys ®). Five streams were obtained and characterised by comparing its different boiling points with conventional fuels. The first stream (7.4 wt%) showed similar characteristics with light naphtha (boiling point range 61.5–107.5 °C). The second stream (22.37 wt%) was comparable to commercial naphtha (146.4–199.5 °C). The third stream (15.18 wt%) coincided with No. 1 fuel–oil regarding boiling point range, flash point and sulphur content. The last two fractions were classified as heavy gas oil according to their boiling point (305.1–363.3 °C and 335.3–374.4 °C respectively). More results reported in literature are shown in Table 11.

According to several authors [12,54,78,112,114,153,182] the naphtha fraction contains high percents of limonene, up to 25 wt% of the naphtha fraction. The analysis of the naphtha fraction obtained by Benallal et al. [114] showed that this fraction had a higher octane number than petroleum naphtha. In this way Roy et al. [149] reported that the light fraction (distilled up to 160 °C) was positively tested as a gasoline additive. They also tested successfully the middle fraction (< 204 °C) of the tyre liquid as a plasticizer in rubbers and highlighted the reduction of the cure time and consequently a higher speed in the vulcanisation process. The heavy fraction (> 350 °C) was also tested for coke production and proposed for road pavements.

4.1.4. *Tyre liquid as alternative fuel in internal combustion engines*

Tyre pyrolysis liquid as alternative fuel in internal combustion engines (ICEs) is a very attractive application given the flexibility of this type of fuels in terms of storage and transportation, as well as the current fossil fuels impacts and their increasing prices. Also, the high energy content of the tyre liquid, the possibility of recycling CO_2 (and consequently the reduction in greenhouse gas emissions) and the high thermal efficiency of diesel engines (the most common ICE available in the present day [188]) offer several advantages from the environmental and energy point of view. However, as stated before, tyre liquid presents a wide distillation range with significant contents of olefinic and aromatic compounds that limit its direct use in ICEs. Among other issues such as sulphur and viscosity, these characteristics give way to both lower flash point and cetane number than standard diesel fuels. Even so, there are some works reported in literature that showed the effect of tyre liquid/diesel fuel blends on engine performance and emission in diesel engines [187–192]. These studies showed different results due to the different properties of the tyre liquid as well as possible engine differences. Under this

Table 12
Some properties of the tyre liquid pyrolysis reported in literature.

Ref.	Tyre characteristics	Pyrolysis conditions		Density at 15 °C (kg/m³)	Kinematic viscosity at 40 °C (cSt)	CV. (MJ/kg)	Cetane number	H/C atomic ratio	Flash point. (°C)	Moisture. (wt%)	pH	Sulphur. (wt%)	Ash. content (wt%)	Carbon residue. (wt%)	Aromatic content. (wt%)	Aliphatic content. (wt%)
[51]	Motorcycle tyre	FBR at 475 °C; atm. pressure		957[b]	4.75[c]	42.00	40[j]	1.27	< 32	–	4.40	1.25	0.22	–	16.65	49.54
[54]	Passenger car tyre	FBR at 500 °C; atm. pressure		–	–	42.10	–	1.44	15	4.40[f]	–	1.30	0.002	–	40.50	47.20
[58]	Scrap tyres. Origen not specified.	Pilot-scale RKR at vacuum conditions[n]	450 °C	941[h]	2.87[d]	41.90[m]	–	1.55	27	0.52	–	0.97	traces	1.36[g]	–	–
			650 °C	982[h]	2.00[d]	41.00[m]	–	1.26	13	0.85	–	1.11	traces	3.26[g]	–	–
[65]	Passenger car tyre	FBR at 425 °C, pressure not reported	Liquid treated[i]	992	6.52	42.70	–	1.37	–	–	–	1.46	–	–	42.32	–
			Liquid without treatment	995	6.61	41.31	–	1.39	–	–	–	1.37	–	–	36.14	–
[66]	A mixture between passenger car and truck tyres	Six vertical. tubular. reactors operated at batch scale at 550 °C; atm pressure		900[b]	2.81	43.27	–	1.60	20	–	–	0.60	–	–	–	–
[69]	Passenger car tyre	FBR	650 °C; atm pressure	943[h]	4.62	41.60	–	1.42	< 30	–	–	1.35	–	–	41.21[f]	–
	Truck tyre		650 °C; atm pressure	913[h]	3.85	42.40	–	1.63	< 30	–	–	0.83	–	–	15.29[f]	–
[118]	A mixture of UK types and grades	Slow pyrolysis in a large capacity reactor. Temperature and pressure not reported		910[h]	6.30	42.10	–	1.28	20	4.60[f]	–	1.45	0.002	2.20	–	–
[149]	Passenger car tyre	Pyrocycling™ process	520 °C; 7 kPa[a]	950[b]	9.70[d]	43.70	–	1.50	28	0.30	–	0.80	traces	1.30[g]	–	–
	Truck tyre		485 °C; 6 kPa[a]	939[b]	17.80[d]	44.80	–	1.53	22	1.50	–	1.00	0.005	1.20[g]	–	–
[187]	Vehicle (tyre type not specified)	FBR at 500 °C[l], pressure not reported		945[b]	3.80	43.34	44	–	50	–	–	0.90	–	–	–	–
[188]	A mixture of passenger car, truck and bike tyres, among others.	Vacuum conditions, temperature not reported	Liquid treated[k]	904	2.16	40.90[m]	< 40	–	60	–	–	0.43	0.0005	1.00	69.70	–
			Liquid without treatment	944	5.06	39.90[m]	–	–	42	–	–	1.13	0.006	21.51	–	–
[189]	Passenger car tyre	FBR heated between 450 and 600 °C, pressure not reported	Liquid treated[e]	871	1.70	45.78	–	–	36	–	–	0.26	–	0.02	–	–
			Liquid without treatment	935	3.20	42.83	–	–	43	–	–	0.95	0.31	2.14	64.00	–

[a] Total pressure.
[b] At 20 °C.
[c] At 30 °C.
[d] At 50 °C.
[e] The liquid was previously treated: removal of moisture, desulphurisation and vacuum distillation.
[f] Percent in volume.
[g] Carbon conradson residue.
[h] Temperature not reported.
[i] Catalytic pyrolysis with expanded perlite.
[j] Extracted from [192].
[k] Pyrolysis temperature not reported, the liquid was previously treated by means of refining and desulphurisation process: hydro-sulphuric acid (H_2SO_4) treatment, activated bentonite–Calcium Oxide (CaO) treatment, vacuum distillation, oxidative desulphurisation, washing and drying;
[l] Catalytic pyrolysis with 5% $Ca(OH)_2$.
[m] Lower calorific value.
[n] Pressure between −10 and −20 Pa.

context, Table 12 summarises different tyre liquid properties reported in literature.

Conventional diesel fuels have a cetane number between 40 and 55 [193] whilst tyre liquid has showed values between 40 [192] and 44 [187]. A low cetane number ($<$ 40) means that the fuel will have a long ignition delay and therefore more fuel than the desirable is injected into the cylinder before the first fuel particles ignite. Hence, a fast and large pressure increase at the start of combustion is achieved. This situation results in a low thermal efficiency and a rough-running engine as well as unacceptable levels of exhaust smoke and emissions [194]. For instance, Ilkilic and Aydin [187] observed that tyre liquid in a direct injection diesel engine produces higher CO, HC, SO_2 and smoke emissions than conventional diesel. The authors attributed this behaviour mainly to the poor atomisation and low cetane number (44). Also, the high density caused/resulted more fuel to be injected in mass base and this led to a rich combustion condition and consequently, to a higher smoke opacity. They concluded that blends of tyre liquid with diesel up to 75 wt% could be efficiently used in diesel engines without any engine modification. Similarly, Murugan et al. [191] observed an increase in the NOx, HC and CO emissions when different blends of tyre liquid and diesel fuel were fuelled in a direct injection diesel engine (up to 70 vol% of tyre pyrolysis liquid). They ascribed this behaviour to the aromatic content, higher viscosity and lower volatility of the fuel. According to Heywood [193] aromatic compounds have poor ignition quality. Cycloalkanes and aromatics generally reduce the cetane number unless they have a long n-alkane chain attached to the ring [193].

Moreover, a high viscosity of the tyre liquid will lead to problems in the long run that could include carbon deposit and oil ring sticking [189] and it affects the fuel flow through pipes, the fuel atomisation and the performance and wear of the fuel pump [4,58]. The high viscosity is linked to the large molecular mass and chemical structure of the tyre liquid compounds [189]. Besides the higher sulphur content, the tyre liquid can present some solid particles of char, sand or alkali metals [154] that can lead to wear problems in the engine pieces and also environmental and health impacts. Murugan et al. [189] also stated the presence of some polymers and tar compounds in the tyre liquid, suggesting the possible effect of carbonaceous formation in the combustion chamber, exhaust valves and ports and also in the piston ring grooves. For this reason, prior to its direct feed in the engine, it is advisory a refining process in order to improve the combustion properties of the tyre liquid [149,189,192]. Under this context, Murugan et al. [189] modified the tyre liquid to reduce the viscosity and sulphur content. The refining process involved three stages: removal of moisture, desulphurisation and vacuum distillation. As consequence, the modified fuel had about 7% higher calorific value than the crude one. The authors observed that the engine was able to run up to 90 vol% of distilled tyre pyrolysis liquid and 10 vol% of diesel fuel and a thermal efficiency de-rating about 1–2% in comparison to diesel fuel was found. Although HC and CO emissions were higher than for conventional diesel fuel (attributed to the presence of unsaturated hydrocarbon), the NOx emissions were lower by about 18% in comparison to diesel fuel. Engine failed to run satisfactorily using 100% of distilled tyre liquid. Likewise, Doğan et al. [188] studied the effect of tyre liquid/diesel fuel blends on both the engine performance and exhaust emissions of a direct injection unmodified diesel engine at full load and at four different engine speeds (1400. 2000. 2600 and 3200 rpm). The pyrolysis process was conducted under vacuum conditions and the tyre liquid was previously treated before its use in the engine. The treatment consisted of a refining and desulphurisation process as follows: hydrosulphuric acid (H_2SO_4) treatment, activated bentonite–calcium oxide (CaO) treatment, vacuum distillation, oxidative desulphurisation and finally washing and drying. The authors did not find major effects on the engine output torque, the engine power, brake specific energy consumption and brake thermal efficiency with respect to those of the reference diesel fuel when the tyre liquid was blended up to 90 vol%. At 100% tyre liquid caused a malfunction at higher engine speeds. The main conclusion was that tyre liquid fuel blends can be used in diesel engines without significant loss in engine performance (up to 70% of tyre liquid) while improving some engine emissions, especially for smoke opacity, CO and HC emissions.

4.2. Char from tyre pyrolysis

Generally speaking, pyrolysis offers the possibility to convert organic matter into a carbon-rich solid (char). For the case of tyres, this solid carbonaceous fraction, also named pyrolytic CB, corresponds to the initial CB as well as the inorganics used in the tyre manufacture such as Zn, Ca and Si [83,168,195]. The char composition depends on the pyrolysis conditions and the tyre composition and its quality and yield greatly influence the WT pyrolysis economic feasibility [62,78] besides the liquid fraction. Temperatures at which a good conversion grade of the tyre is ensured ($\sim$500 °C), pyrolytic CB represents approximately 35–40 wt% (fixed carbon plus ash content) or even lower values depending on the tyre composition. In addition, it can contain some extra carbonaceous material as consequence of repolymerisation reactions among the polymer-derivates depending on the process severity and complexity [50,63,149,195,196]. Therefore, some of the organic vapours released during pyrolysis are converted into coke by dealkylation and dehydrogenation reactions or absorbed on the char surface [62,156,178]. For this reason, it is expected that pyrolytic CB shows much coarser particle sizes than the original CB as stated by Senneca et al. [61]. According to the authors, these findings suggest that CB particles are likely to act as nuclei seed where coherent solid carbon structures grow (by cyclisation and/or crosslinking). This extra-carbon is also evidenced when the pyrolytic CB is further activated with steam or CO_2. Thus, two different reaction rates can be found: a higher rate of weight loss at low degrees of burn-off where the carbonaceous deposits are released and a slower second stage characterised by a linear period of burn-off, where the char gasification takes place [197–199]. On the other hand, the char yield obtained after vacuum pyrolysis gives a similar carbon concentration of a virgin CB since lower pressures limit the hydrocarbon adsorption on the CB surface (secondary reaction) as commented before. According to Roy works [83] this char appear to be comparable to commercial CBs of the N300 series.

One of the most immediate uses of the pyrolytic CB is the production of activated carbon as shown by several authors [196,200–202]. In fact, there is a comprehensive review about this topic [203] that stated that activated carbons with BET surface areas up to 1000 m^2/g have been produced from WT using steam and CO_2. Other minor applications are as reinforcing filler for low-value rubber goods, as filler in road pavement, printing ink pigment or used blended with bitumen in order to improve its rheological properties. More information can be found elsewhere [83].

Moreover, pyrolytic CB can present a calorific value between 25 and 34 MJ/kg (Table 13) that makes it very attractive as a solid fuel. Depending on the experimental conditions, tyre composition and technology used in the pyrolysis process, pyrolytic CB may have compositions of carbon and sulphur higher than 80 and 3 wt% respectively. Table 13 shows a compendium of char yield, calorific value and sulphur content for different results reported in literature. According to Aylón [185] pyrolytic CB is a low reactivity material with slow oxidation kinetic. Therefore, pyrolytic CB combustion implies longer residence times at elevated temperatures. Moreover, given the low particle size and the bulk density of the pyrolytic CB, a

Table 13
Elemental, proximate and calorific value of the char fraction reported in literature.

Char yield (wt%)	Elemental analysis on dry basis (wt%)				Proximate analysis on as received basis (wt%)				CV (MJ/kg)	Sulphur in tyre (wt%)	Sulphur retention (wt%)	BET surface (m^2/g)	Pyrolysis temperature (°C)	Reactor type	Ref.
	C	H	N	S	A	VM	FC	M							
37.90[e]	82.70	0.40	< 1	2.20	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	–	69.50	500	FBR	[16]
37.60	n.r.	n.r.	n.r.	n.r.	16.10	5.50	78.40	0.00	27.90[f]	1.40	n.r.	n.r.	550	FBR	[56]
39.90	80.82	1.46	0.53	2.41	14.58	6.92	77.22	1.28	30.00[g]	1.53	62.85	89.10	550	RKR	[58]
36.10	85.18	1.15	0.64	2.03	13.25	n.r.	n.r.	n.r.	n.r.	0.92	79.66	67.96	500	FBR	[62]
38.00	90.27	0.26	0.16	1.22	8.41	0.67	90.80	0.09	n.r.	1.38	33.59	63.00	500	FBR	[63]
40.00[b]	86.30	0.30	0.30	2.80	12.50	1.80	91.30	0.40	29.70[f]	1.81	61.88	64	550	FBR[a]	[66]
33.00	80.08	0.42	0.17	2.84	16.50	1.20	81.30	1.00	28.57[f]	1.77	52.93	n.r.	550	FBR	[68]
41.70[c]	n.r.	n.r.	n.r.	1.00	40.80	n.r.	55.90	n.r.	15.70[f]	1.71	24.39	60.50	650	FBR	[69]
33.80[d]	n.r.	n.r.	n.r.	2.30	14.80	n.r.	82.60	n.r.	33.40[f]	1.44	53.99	63.50			
49.09	85.31	1.77	0.34	2.13	15.33	12.78	71.89	3.57	30.71[f]	2.30	45.46	n.r.	550	RKR	[138]
35.00	89.40	0.30	1.80	0.90	7.70	n.r.	n.r.	n.r.	30.90[h]	1.70	18.53	n.r.	550	FBR	[153]
52.50	0.00	0.00	0.00	2.59	n.r.	n.r.	n.r.	n.r.	n.r.	1.60	84.98	n.r.	550	FBR	[156]
34.05[c]	86.62	1.39	0.75	2.24	n.r.	n.r.	n.r.	n.r.	n.r.	2.14	35.64	65.20	500	CSBR	[167]
36.92[d]	87.36	0.91	0.44	3.29	n.r.	n.r.	n.r.	n.r.	n.r.	2.00	60.73	77.90			
38.00	82.10	0.97	0.35	3.41	13.17	3.5	82.09	1.2.4	n.r.	1.87	69.29	n.r.	600	AR	[179]
	81.78	0.84	0.33	2.96	13.82	2.51	83.41	0.26	n.r.		60.10	n.r.		FBR	
57.83	n.r.	n.r.	n.r.	2.51	n.r.	n.r.	n.r.	n.r.	n.r.	1.57	92.35	n.r.	Thermal plasma pyrolysis		[206]

n.r., not reported; n.d., not detectable; A: ash; VM: volatile matter; FC: fixed carbon; M: moisture.

[a] Distillation plant consisting of six vertical. tubular. stainless steel reactor.
[b] Mixture between passenger car and truck tyres.
[c] Passenger car tyre.
[d] Truck tyre.
[e] Mixture of different tyre brands.
[f] Higher.
[g] Not specified.
[h] Lower.

Table 14
Some types of carbon black used in tyres [208].

Name	Abbrev.	ASTM Design	Particle size (nm)	Tensile strength (MPa)	Relative laboratory abrasion	Relative roadwear abrasion
Super abrasion furnace	SAF	N110	20–25	25.20	1.35	1.25
Intermediate SAF	ISAF	N220	24–33	23.10	1.25	1.15
High abrasion furnace	HAF	N330	28–36	22.4	1.00	1.00
Easy processing channel	EPC	N300	30–35	21.7	0.80	0.90
Fast extruding furnace	FEF	N550	39–55	18.2	0.64	0.72
High modulus furnace	HMF	N683	49–73	16.1	0.56	0.66
Semi-reinforcing furnace	SRF	N770	70–96	14.7	0.48	0.60
Fine thermal	FT	N880	180–200	12.6	0.22	–
Medium thermal	MT	N990	250–350	9.8	0.18	–

high percentage of unburned particles may be found using conventional combustion reactors. Also, the poor volatile content causes a heterogeneous gas–solid reaction with no flame formation. For these reasons combustion of pyrolytic CB is rarely found.

An ideal process for the pyrolytic CB is the rubber manufacture. However, a typical pyrolytic CB cannot be reused as a pure CB due to the high concentration of inorganic impurities [185,204] and particle structure (aggregation degree) [56], despite Faulkner and Weinecke [205] described a pyrolytic CB obtained in a continuous pilot kiln with similar properties of a medium-grade CB in terms of dibutylphthalate and iodine absorption, toluene discoloration, BET surface area and average particle size. This fact reflects the great influence of the tyre feedstock regarding the wide heterogeneity of the virgin CB, which could be the reason of its limit marketability in the commercial sector. In this way, several and different conclusions are found in literature and all of them could be ascribed to the pyrolysis conditions and the various grades and characteristics of commercial CB used in tyre manufacture. For instance, Williams et al. [52] using a FBR reported that the surface area of the pyrolytic CB can increase with both pyrolysis temperature and heating rate. Similarly, Kawakami et a1. [47] showed that the physical properties of the pyrolytic CB produced in a RKR such as tensile strength, elongation and hardness, mainly depend on the pyrolysis temperature. Kaminsky et al. [170] using a BFBR found pyrolytic CB with less porosity than the original CB working at temperatures between 700 and 790 °C. Zhang et al. [62] in a FBR under vacuum pressure reported BET surface area around 68 m^2/g. They highlighted that this value is in the middle of the surface areas of commercial CBs of the N550 and N600 series, which are approximately around 45 and 90 m^2/g respectively.

Manufacturing tyre rubber from pyrolytic CB also needs a suitable surface chemistry and activity since these properties determine the strength of the carbon black–rubber interaction [83,149]. In spite of this, the mineral content seems to be the most important characteristic as commented above. These compounds can be removed applying a demineralization process as reported by Chaala et al. [195]. Ash concentrations lower than 1 wt% can be obtained after successive acid/base treatments [83]. The most popular CB by far for rubber manufacture is the one

made by the furnace process, with grades ranging from N100 through N700 series [207]. Table 14 [208] shows some properties and characteristics of some CBs used in tyre manufacture.

As final conclusion, there are many barriers regarding the recovery of pyrolytic CB and for this reason the economic feasibility of the WT pyrolysis process has been also limited. Despite pyrolytic CB is a carbonaceous material with higher carbon concentration (> 80 wt%), it continues being a very heterogeneous material regarding the ash content, particle size, absorption properties, structure and both surface chemistry and activity. This is because the tyre manufacture usually uses various grades of commercial CBs and also the complexity of the pyrolysis process which modify the initial characteristic of the virgin CB.

4.3. *Gas from tyre pyrolysis*

The gas remaining after liquid recovery, called pyrolytic gas or pyrogas or sometimes syngas, is typically composed of paraffins and olefins compounds with carbon numbers from one to five [18]. Gross tyre pyrolysis gases are mainly composed of hydrogen (H_2), carbon monoxide (CO), carbon dioxide (CO_2), methane (CH_4), ethane (C_2H_6), ethene (C_2H_4), propane (C_3H_8), propene (C_3H_6), butane (C_4H_{10}), butenes (C_4H_8) and butadiene (C_4H_6), and some low concentrations of sulphur (H_2S, SO_2, COS, CS_2) and nitrogen (NH_3) compounds [62,200]. The presence of C_4 compounds is mainly ascribed to BR and SBR thermal degradation. Table 15 shows a compendium of the gas composition, calorific value and yield reported by several authors. As pointed by Aylón et al. [179] the gas composition is not only affected by the reaction temperature but also by the raw material and the experimental installation that can lead to some secondary reactions. The authors observed some differences between the results obtained from the FBR and the AR both at 600 °C. In the case of the AR, the percentage corresponding to the lightest compounds was higher than in the FBR. The more severe cracking of the products in the AR was attributed to the faster heating rate and longer volatiles

Table 15
Composition and calorific value of the gas fraction reported in literature.

Gas yield (wt%)	CV (MJ/Nm^3)	Gas concentration (vol%)												Pyrolysis temperature (°C)	Reactor type	Ref.
		H_2	CO	CO_2	CH_4	C_2H_6	C_2H_4	C_2H_2	C_3	C_4	C_5	C_6	H_2S			
2.40[p]	30.30[d]	21.50	5.10	26.20	17.30	8.20	8.70	n.r.	7.30[a]	5.70[q]	n.r.	n.r.	n.r.	500	FBR	[16]
17.20	75.50[d]	n.r.	4.80	9.40	19.80	9.10	9.40	n.r.	10.80[a]	21.30[e]	7.60[ab]	2.80[ac]	n.r.	500	FBR	[50]
25.50	38.10	20.70	2.60	1.80	44.50	4.40	17.30	n.r.	3.90	1.30	n.r.	n.r.	n.r.	800	FBR	[57]
13.90[ad]	68.70[d]	22.27	1.98	2.54	21.32	4.19	2.32	n.r.	5.43[a]	35.39[h]	< 2		n.d.	550	FBR[a]	[66]
29.00	36.16[c]	40.00	1.60	1.40	26.00	20.00		n.r.	6.00[i]	2.80[j]	1.10	0.10	n.r.	550	FBR	[68]
7.60[k]	n.r.	26.06	1.15	2.41	23.92[m]	13.37[n]			11.80	7.64	10.74	0.19	4.18	650	FBR	[69]
7.60[l]	n.r.	19.09	2.02	6.08	24.21[m]	16.99[n]			12.56	9.53	12.20	0.22	0.94			
3.80	8.55[c]	17.86	0.26	0.78	5.64	1.75	0.833	0.00	1.49[a]	1.95[e]	0.021[f]	0.30[g]	0.045	550	FBR	[156]
4.25[k]	n.r.	0	n.r.	0.002	0.19	0.16	0.49	n.r.	0.67[a]	2.48[o]	n.r.	n.r.	n.r.	500	CSBR	[167]
2.18[l]	n.r.	0	n.r.	0.002	0.21	0.10	0.40	n.r.	0.71[a]	0.47[o]	n.r.	n.r.	n.r.			
20.90[r]	n.r.	0.80	t	t	10.20	n.r.	2.60	n.r.	0.70[i]	0.30[u]	n.r.	n.r.	1.60	740	BFBR[v]	[170]
28.50[s]	n.r.	1.30	3.80	2.00	10.10	n.r.	4.00	n.r.	2.50[i]	0.20[u]	n.r.	n.r.	0.20	750	BFBR[w]	
29.40[s]	n.r.	0.70	t	t	10.10	n.r.	9.00	n.r.	3.50[i]	1.40[u]	n.r.	n.r.	0.01	780	BFBR[w]	
19.00[t]	n.r.	0.40	1.50	1.70	6.10	n.r.	1.70	n.r.	1.50[i]	0.30[u]	n.r.	n.r.	0.02	700	BFBR[x]	
4.00	65.60[d]	7.90	9.00[y]		9.90[z]	5.90[aa]			5.30	38.10	n.r.	n.r.	2.90	550	FBR	[173]
17.10	n.r.	38.30	1.80	2.30	19.60	5.40	5.70	n.r.	3.90[a]	6.60[b]	n.r.	n.r.	2.20	600	AR	[179]
7.50	n.r.	30.40	2.38	2.90	23.27	6.20	4.45	n.r.	7.65[a]	10.74[b]	n.r.	n.r.	1.55		FBR	

n.r., not reported; n.d., not detectable; t, traces.

[a] Propane + propene.
[b] Iso-butane + butane + trans-2-butene + 1 butane + isobutene + c2-butene + 1.3-butadiene.
[c] Lower.
[d] Higher.
[e] Butane + butene + isobutylene + butadiene.
[f] *cis*-Pentene.
[g] *n*-Hexane + cyclohexane.
[h] 2-Butene + *n*-butane + *i*-butane.
[i] Propene.
[j] Butadiene and remaining C_4.
[k] Passenger car tyre.
[l] Truck tyre.
[m] As C_1.
[n] As C_2 and C_2═.
[o] Isobutene + 1.3-butadiene + 2-butene.
[p] Mixture of different tyre brands.
[q] Butane + 2-butene + 1.3-butadiene.
[r] Tyre powder.
[s] Tyre pieces.
[t] Whole pieces.
[u] Butadiene.
[v] Laboratory fluidised bed plant (throughput of 1 kg/h).
[w] Technical fluidised bed plant (throughput of 30 kg/h).
[x] Pilot fluidised bed (throughput of 200 kg/h).
[y] As Cox.
[z] As C_1.
[aa] As C_2.
[ab] Pentene + pentane.
[ac] Hexane + hexane.
[ad] Distance between passenger car and truck tyres.

residence time in this type of reactor. Similar results were reported by Díez et al. [159] using a FBR and a batch moving bed pilot plant. In the same way, Galvagno et al. [138] reported a calorific value around 22 MJ/kg when the process was carried out at 550 °C and 29 MJ/kg when process temperature increased up to 680 °C. This study was carried out in a RKR externally heated (110 dm^3 in volume and 0.4 m in diameter) under light overpressure (maximum working pressure of 300 mm w.c.). Roy and Unswoth [110] reported a gross calorific value of 36.8 MJ/kg with an average molecular weight of 28.3 using a FBR at 415 °C. Likewise, Laresgoiti et al. [169] found that tyre pyrolysis gases obtained in a autoclave reactor under N_2 atmosphere was around 81 MJ/m^3 when the process was carried out at 400 °C and 69.5 MJ/Nm^3 at 700 °C, both values after 30 min of pyrolysis reaction time. Ucar et al. [69] reported a gross calorific value about 60–65 MJ/Nm^3 for both PCT and TT pyrolysis using a FBR at 650 °C. Sulphur compounds concentration, mainly H_2S, was higher in PCT than TT although the sulphur content in both types of tyres was similar. More detailed information about the gas properties from WT pyrolysis is shown in Table 15.

The most frequent use for the gas fraction must be to supply the heat required by the process. Under this context, Kaminsky and Sinn [102] using a BFBR found that the process was self-sufficient regarding energy needs. Similar results have been pointed out for several authors using different technologies [4,57,83,138,149,169,209].

5. Conclusions

The literature on thermochemical treatment of pyrolysis applied to WT has been widely surveyed. WT pyrolysis has received special attention from 1990s although since late 1960s a remarkable number of projects with a broad range of technologies and scales can also be found. Pyrolysis seems to be more attractive in comparison with other thermochemical processes to tackle the WT disposal problem because of its minor environmental impact and the recovery of solid and liquid material. The BFBR, CFBR, CSBR, RKR and AR are the main technologies available for the pyrolysis commercialisation at pilot/industrial scale. However, currently WT pyrolysis is mainly engaged in research purposes. An important disadvantage is the legislative barriers because pyrolysis is classified as incineration in the EU and this discourages its public acceptance. From the technical point of view, one noteworthy limitation for industrial plants is the difficulty of transferring the heat efficiently to drive the pyrolysis process in such a way that the temperature is evenly distributed. Similarly, the absence of a wide market mainly for the solid fraction has caused that WT pyrolysis is not yet industrially widespread. The quality of CB and the price of tyre liquid play a very important role. For this reason, much research is being carried out at the moment to overcome these drawbacks in the current context of both dependency and fossil fuel depletion.

Regarding the WT as a fuel feedstock, it is worth noting that:

- Generally speaking, vehicle tyres comprise PCT, TT and MT. All of them exhibit different proportions of NR, SR (BR and SBR), CB and fillers. PCT and TT have a high calorific value (35–40 MJ/kg), even greater than most of the conventional fuels used in power plants. MT has a low calorific value that normally does not exceed 30 MJ/kg because the lower volatile fraction (~58 wt%) as well as the higher ash content (~20 wt%).
- Taking into account the NR content in the WT, the CO_2 fossil emission per unit of energy is less than coal and petroleum offering potential reductions in greenhouse gas emissions. For instance, assuming a 30 wt% of NR in the WT, the combustion of the volatile fraction released in WT pyrolysis gives 136.51 gCO_2/kW h, which is lower than some fossil fuels usually used in power generation. Differences account for 167%, 159% and 48% for lignite, crude oil and natural gas respectively.

Regarding the WT pyrolysis, it is worth mentioning that:

- Rubber degradation begins to be appreciable around 200 °C and above this temperature significant yields of volatiles are released. Generally speaking it is possible to say that NR decomposes first (~380 °C), followed by SBR (~450 °C) and BR (~460 °C).
- Five hundred degree celsius appears to be the optimum temperature to carry out WT pyrolysis, at atmospheric pressure, since total tyre conversion is achieved. At lower temperatures, some rubber tyre compounds still remain in the pyrolytic CB, showing a heterogeneous sticky-gummy aspect. Even though temperature is the main governing variable, the final effect is accompanied by other variables involved on the process such as pressure, heating rate and superficial velocity of the carrier gas. From the large number of works published in the subject, three different behaviours for the pyrolysis yields behaviour as a function of temperature have been proposed and analysed in this review. Type I represents the normal behaviour of pyrolysis without secondary reactions. Type II is the pyrolysis process with secondary reactions that involve both liquid and gas fractions, whilst solid fraction remains constant. Type III corresponds to the usual behaviour for processes with vigorous gas–solid contact that encourage secondary reactions increasing both the solid and the gas fraction yield.
- A pressure increase leads to more viscous liquid product with a higher coking tendency. In contrast, a lower pressure induces lower temperatures for performing the pyrolysis process and therefore the thermal energy demand is reduced. Generally speaking, vacuum pyrolysis reduces the occurrence of secondary reactions and helps to reduce the mass flow rate of the inert gas.
- The composition of the WT has a direct effect on the quality of the resultant products as well as the final product distribution. Tyre rubber with higher SBR composition (and consequently lower NR) as PCT gives higher amounts of aromatic hydrocarbons in the pyrolytic liquid. The styrene product after WT pyrolysis is also related to the SBR content in the tyre. In contrast, it is expected that a tyre feedstock with a higher NR content gives way to a higher limonene concentration.
- The tyre particle size and the pyrolysis conversion are inversely related. Particle size effect on tyre pyrolysis mainly depends on the heating rate, temperature, pressure, pyrolysis reaction time and volatiles residence time since all this variables influence the occurrence of secondary reactions. Even so, it appears that as the heating rate increases, the process can be conducted with higher particle sizes.
- The heating rate affects the degradation rate as well as the temperature at which maximum devolatilisation begins and ends. Characteristics of the vapours released in the pyrolysis process are also affected and the balance between primary and secondary devolatilisation products depends on the interaction between heating rate and particle size. Low heating rates may conduct to some resistance to mass or heat transfer inside the particle. Higher heating rates promote a better heat and mass transfer mechanism.

- The presence of an inert gas in the pyrolysis process allows controlling the occurrence of secondary reactions and also guaranteeing the absence of oxygen that could lead to some kind of oxidation. As the flow rate increases the superficial gas velocity increases and consequently the vapour residence time decreases. The carrier gas seems the key variable to control the appearance of secondary reactions when the pyrolysis process is carried out under atmospheric pressure.
- Pyrolysis time is a key factor in order to scale up an industrial system that depends on the particle size and the reactor technology. Lower residence time involves lower reactor volumes and therefore lower cost of the system. Generally speaking, it is expected that bigger particles need longer reaction times than smaller ones to reach the same pyrolysis conversion grade. Even so, both longer pyrolysis time and higher temperature negatively affect to the quantity of heat required to complete the pyrolysis and consequently the process efficiency.
- Liquid from tyre pyrolysis can reach 44 MJ/kg of energy content depending on the tyre composition and the process conditions and has comparable properties to that of petroleum diesel. It generally presents a very small amount of oxygen content and a high H/C atomic ratio (around 1.5) representative of aliphatic and aromatic compounds. A typical distillation curve shows a mixture of gasoline and diesel fuels with a wide range of boiling points ($\sim$70 and 400 °C) that consequently reflects the fact that the tyre liquid is an unrefined hydrocarbon.
- Limonene is the main product of the liquid fraction when no secondary reactions take place and its production decreases as temperature increases due to the rise of secondary reactions. Limonene yield is mainly related to the polyisoprene rubber (NR) present in tyre.
- Diels–Alder reaction seems to be the mean mechanism to explain the formation of PAHs and the increase in the aromatisation grade in the tyre liquid as the pyrolysis temperature increases. However, it is worth pointing out that this occurs as long as secondary reactions take place. Even so, tyre composition also influence the PAHs concentration since SBR seems to be the main precursor for PAH formation.
- Secondary reactions are linked with many variables involved in the pyrolysis process. The reactor type, which also determines both the characteristics of the heat transfer and the residence time of the volatiles and solids (pyrolysis time), exerts a notably role.
- Despite pyrolytic CB is a carbonaceous material with higher carbon concentration ($>$80 wt%), it is a very heterogeneous material regarding the ash content, particle size, absorption properties, structure and both surface chemistry and activity. All these variables affect its recovery and consequently, the economic feasibility of the WT pyrolysis process.

Acknowledgements

This study has been carried out under the framework of the TRACE PET2008_0103 project financed by the Spanish Ministry of Science and Innovation. JDM thanks Fundación Carolina for the fellowship as well as the Enlaza-Mundos Program.

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